



Risk assessment of harmful types of plastics in the marine environment

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Abstract:	This report presents the results of a risk assessment of residual chemical additives, monomers and degradation products present in microplastic (MP) particles in the marine environment. Seven cases of different polymer types and product groups are defined that represent the most significant exposures of MPs, and thus potential high-risk cases towards marine organisms. Risk Quotients (RQ) are calculated for three trophic levels, i.e. pelagic/planktonic zooplankton: copepod, benthopelagic fish: atlantic cod and seabird: northern fulmar. Danish <i>Miljøkvalitetskrav</i> (MKK) and European Environmental Quality Standard (EQS) values are used as toxicity threshold values. RQ larger than unity, which indicates potential risk, is estimated for copepod and cod (pelagic community) and the flame-retardant pentabromodiphenylether (PeBDE) used in polyurethane (PUR), the biocide tributyltin (TBT) used in polyvinylchloride (PVC) and PUR, and the flame-retardant hexabromocyclododecane (HBCD) used in expanded polystyrene (EPS). The highest estimated RQ for fulmar (secondary poisoning) is 0.1 for PeBDE used in PUR.
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Preface

This report synthesizes knowledge on the potentially most environmentally harmful types of microplastics (MP) with respect to their chemical additives, residual monomers and degradation products. At present, the environmental impacts of different types of MP are dealt with as one group – microplastics. Some types are however more harmful than others and an identification of the more environmentally harmful MP and associated chemicals are important in terms of risk assessment and risk management of additives and plastic products that are relevant to the marine environment. This report identifies the potentially more harmful types of MP based on knowledge of production, chemical composition (additives), usage, emission fate and occurrence and ecotoxicological effects. A risk assessment towards relevant marine species is carried out for the residual additives, monomers and degradation products of these MP. An important point is to outline a procedure for performing such a risk assessment and highlight the availability of data and missing data that are needed to improve the marine risk assessment.

Sammenfatning

I denne rapport præsenteres resultaterne af en risikovurdering af rester af additiver, monomerer og nedbrydningsprodukter, som forekommer i plastik (mikro)partikler i det marine miljø. Det er ikke en udtømmende risikovurdering af kemiske additiver men snarere et eksempel på en fremgangsmåde, hvor viden og data anvendes for rapporterede additiver, der er repræsentative for specifikke plastiktyster og produkter, der bliver anvendt i Danmark. Risikotilgangen belyser kæden fra plastfremstilling til effekter, via skæbnen i miljøet og optaget i organismerne. Risikovurderingen omfatter vandrammedirektivets prioriterede stoffer og visse andre forurenende stoffer.

Et pionerstudie om flokkulering af suspensioner, der både indeholder naturligt forekommende sediment og mikroplastik (MP) partikler blev udført som en del af projektet. Forsøgene viste betydelig flokkulering og ingen fraktionering af MP partiklerne sammenlignet med de øvrige suspenderede partikler. Resultaterne er lovende og peger på, at der er et behov for videre studier, der anvender en kombination af naturlige partikler og MP partikler i miljømæssigt relevante koncentrationer.

Projektet har bidraget til ny viden inden for sedimentering af partikler fra *dolly ropes* og betydningen af flokkulering af MP. Endvidere er modeller blevet videreudviklet, som kan indgå i det videre arbejde samt deles med forskere inden for området. Studierne har også bidraget til en øget forståelse af hvilke elementer af bio-coating, der med fordel kan undersøges fremover.

Forsøg er blevet udført til at undersøge effekten af potentielt skadelige MP partikler på kystnært zooplankton. Vandlopper blev eksponeret for stigende koncentrationer af nye og brugte dæk partikler samt fyld fra kunstgræs baner, der er lavet af brugte dæk. Disse blev formålet til partikelstørrelser svarende til zooplankton føde. Resultaterne vist ingen stigning i dødelighed eller fald i reproduktionskapacitet ved eller under 10 000 plastikpartikler per L, uanset plastik type, zooplankton art eller føde niveau. MP koncentrationer i danske kystnære områder er væsentligt lavere og korttids effekter skønnes derfor at være begrænsede.

Analytiske metoder er diskuteret og konklusionen er, at der stadig ikke er konsensus om, hvilke teknikker der skal anvendes til prøvetagning og analyse. På nuværende tidspunkt er μ FTIR en af de mest anvendte metoder til at identificere MP præcist og hurtigt. Der bruges dog en række forskellige metoder afhængig af det tilgængelige udstyr, hvilket komplicerer en entydig sammenlignelig kvantificering af MP koncentrationer samt bestemmelse af polymer sammensætningen mellem områder og over tid. Følgelig er der et behov for at udvikle standardiserede metoder til monitorering og også at identificere indikatorer til at definere MP effekter i miljøet.

Problemet vedrørende plastpartikler i nanostørrelse er diskuteret og endelig diskuteres hvilke data og hvilken viden der er nødvendig for at forbedre risikovurderingen af MP i det marine miljø.

Risikovurdering

I samarbejde med plastindustrien er der defineret syv cases bestående af forskellige plastpolymerer, der repræsenterer de mest betydende eksponeringer af MP og tilknyttede kemikalier, og derfor også de cases der potentielt giver højest risiko for marine organismer. For hver af disse cases er der tillige identificeret produkttyper med signifikant frigivelse til det marine miljø:

- Lav-densitet polyethylen (LDPE): Plastikposer, beholdere, flasker, rør og produkter til personlig hygiejne.
- Styren butadien gummi (SBR): Bildæk.
- Acrylat polymer (acryl, polyacrylater): Skibsmaling.
- Polyvinyl chlorid (PVC): Kabler, ledninger, linoleumsgulve også på skibe.
- Polyurethan (PUR) stift skum: Bygningsisolering, konstruktionsmaterialer.
- Ekspanderet polystyren (EPS) skum: Bygningsisolering og emballage.
- Polycarbonat (PC): Konstruktionsmaterialer.

Talrige kemiske additiver tilsættes under fremstillingen af plastik, heriblandt funktionelle additiver som flammehæmmere, blødgørere og biocider. Andre additiver giver farve, fyld og styrke til plastikmaterialerne. Nogle additiver har været brugt historisk, men er nu forbudt. De kan dog stadig forefindes i ældre produkter og importerede produkter.

Det kan være svært, hvis ikke umuligt, at få de ønskede data på typer og mængder af additiver i plast. En af grundene er, at alle råmaterialer, der bliver brugt i Danmark, er importerede. En anden vigtig grund er konfidentialitet af data. Derudover forekommer de fleste additiver i små mængder <1-2 wt-% og derfor er det ikke et krav, at de er inkluderet i sikkerhedsdatablade for produkterne. I dette studie er data indhentet fra den videnskabelige litteratur, databaser, rapporter, diverse informationer på internettet samt ved kommunikation med plastindustrien.

Under plastfremstillingen genererer nogle typer plastik betydeligt indhold af ureagerede monomerer samt oligomerer. Nogle monomerer er klassificeret som skadelige. For de betragtede cases er estimeret følgende rest koncentrationer af monomerer: 0.1wt-% ethylen (LDPE); 0.1wt-% 1,3-butadien og 0.1wt-% styren (SBR); 0.01wt-% acrylsyre (acrylmaling); 0.000001wt-% vinyl chlorid (PVC); ingen rest monomerer (PUR); 0.5wt-% styren (EPS); 0.1wt-% bisphenol A (PC).

I en kontekst af MP er risiko ikke kun bestemt af koncentrationen og giftigheden af et kemikalie i miljøet. Risiko afhænger desuden af de specifikke karakteristika ved en MP partikel, der har været udsat for nedbrydning (*weathering*) i miljøet. I dette studie er der ikke set på giftigheden af selve polymer materialet, ligesom kemikalier der er sorberet fra det omgivende miljø (vektor effekten) heller ikke er betragtet. Risikovurderingen er for restmængder af additiver, monomerer samt nedbrydningsprodukter. Den anvendte metode følger fremgangsmåden beskrevet i European Chemicals Agency's (ECHA) retningslinjer i Technical Guidance Document (TGD).

Risiko er beregnet for tre trofiske niveauer af marine organismer, dvs pelagisk zooplankton: vandloppe (*Copepoda*), benthopelagisk fisk: atlantisk torsk (*Gadus morhua*) og havfugl: mallebuk (*Fulmarus glacialis*). For vandlopper sker eksponeringen via det marine vand, for torsk via marint vand og føde-

indtag og for mallemuk via fødeindtag som topprædator og ved direkte indtag af plastpartikler på havoverfladen. Eksponeringskoncentrationen, Predicted Exposure Concentrations (PEC), er bestemt af højest målte koncentrationer af MP i havvand samt fra målte og estimerede mikro- og makro plastmængder i organismernes mave/fordøjelsessystem:

- PEC (MP i marint vand): 42 mgMP/m³
- Torsk: 3.5 µgMP/kgbw/dag og 700 µgMP/kgføde
- Mallemuk: 1 gplastik/kgbw/dag og 3430 µgplastik/kgføde

Som *Predicted No-Effect Concentrations* (PNEC) er anvendt nationalt fastsatte miljøkvalitetskrav (MKK) for andet overfladevand, i henhold til BEK nr 1625 af 19/12/2017, samt EU-fastsatte miljøkvalitetskrav for andet overfladevand, *European Environmental Quality Standard* (EQS) i henhold til Direktiv 2013/39/EU, for vandrammedirektivets prioriterede stoffer og visse andre forurenende stoffer. Herudover er der suppleret med værdier for EQS for fødeindtag (sekundær forgiftning) fra EU 2005 og 2011 dossierer, som danner grundlag for de europæiske EQS værdier for vandrammedirektivets prioriterede stoffer og visse andre stoffer. Når specifikke EQS værdier er tilgængelige for fødeindtag for fisk, anvendes disse for torsk, ellers anvendes MKK/EQS værdien for marint vand for pelagiske arter.

I erkendelsen af at data er begrænsede, er skæbne og eksponerings scenarier udformet, der beskriver de væsentligste processer og parametre med bedst mulige tilgængelige data. Maksimum målte og estimerede mængder af indtagne makro- og MP-partikler i mave/fordøjelsessystem i mallemuk og torsk er anvendt til bestemmelse af eksponering. Det antages, at de indtagne partikler består af én type plastik ad gangen. Mængden af resterende monomerer, additiver og nedbrydningsprodukter efter nedbrydning (*weathering*), svarende til partiklerne i organismernes mave, antages at være 10%. Opløsningsmidler og flygtige stoffer antages ikke at være tilstede. Endvidere antages det, at 10% af de resterende mængder er biotilgængelige.

I de valgte scenarier for skæbne-eksponering-optag er der således nogle antagelser, der kan beskrives som dækkende for de værst tænkelige udfald (*worst-case*), såsom antagelsen om at kun én type polymer udgør hele plast massen. Andre antagelser er tilpasset, så de sandsynligvis er mere realistiske, f.eks. den biotilgængelige fraktion.

17 af ca. 50 identificerede kemikalier har MKK eller EU-EQS værdier, og dermed estimerede PNEC, og indgår derfor i risikovurderingen. Da der antages additivitet af risiko for de enkelte kemikalier, er den samlede sum af risikoefficienterne (RQ), beregnet som PEC/PNEC, derfor underestimeret. Omfanget af underestimeringen kendes dog ikke.

En potentiel risiko, dvs. RQ>1, er fundet for vandloppe og torsk for flammehæmmeren pentabromdiphenylether (PeBDE), der anvendes i PUR, og for biocidet tributyltin (TBT), der anvendes i PVC og PUR, samt for flammehæmmeren hexabromocyclododecan (HBCD), der anvendes i EPS. Den højeste estimerede RQ for mallemuk er på 0.1 for PeBDE, der anvendes i PUR.

Produktionen af PeBDE ophørte i 1997 i EU. Den mest forekommende anvendelse, svarende til 95-98% af produceret PeBDE siden 1999, har været i PUR, hvor PeBDE indholdet er mellem 10 og 18 wt-%. Anvendelsen af PeBDE blev

forbudt i EU i 2004 gennem *Council directive 2003/11/EC* vedrørende restriktioner om markedsføring og anvendelse af visse farlige stoffer. Genanvendelse af produkter der indeholder disse stoffer, der er produceret før indførsel af forbuddet, kan ikke udelukkes.

TBT kan forekomme som urenheder i mono-og dibutyltin stabilisatorer i op til 1wt-%, men indholdet var frivilligt reguleret af industrien til at være ≤ 0.67 wt-% (som tin). Fra juli 2010 er nye produkter med >0.1 wt-% (som tin) forbudt.

HBCD er listet i Stockholm Konventionens Anneks A, med en speciel undtagelse for produktion og anvendelse som flammehæmmer i EPS og XPS i bygninger indtil august 2017. Efter denne dato kan HBCD i EPS og XPS stadig forekomme i miljøet, og betydelige mængder af HBCD kan forekomme i genanvendt PS emballage.

Et andet kemikalie med en relativt højt estimeret RQ (0.1) for vandloppe og torsk er blødgøreren bis-(2-ethylhexyl)phthalate (DEHP), der anvendes i PVC.

For de resterende additiver, dvs. metaller og organiske forbindelser, monomerer, og methylen dianilin (MDA), et nedbrydningsprodukt af methylen diphenyl diisocyanat (MDI), der anvendes i PUR, er de estimerede RQ for individuelle og summerede kemikalier alle under 0.08, hvilket indikerer en yderligere sikkerhedsmargin i forhold til de gængse konservative estimater præsenteret i denne rapport.

Den præsenterede risikovurdering for rester af tilsatte kemikalier og nedbrydningsprodukter i plast er et af de første skridt til at kortlægge de potentielle risici af MP i det marine miljø. En bedre forståelse og beskrivelse af processer for produktion, skæbne, optag og effekter er i høj grad nødvendig. Vigtige datamangler bør fortsat afdækkes. Anbefalinger til fremtidig arbejde er derfor listet i denne rapports afsluttende diskussionsafsnit.

Summary

This report presents the results of a risk assessment of chemical additives, monomer residuals and degradation products that are present in plastic (micro) particles in the marine environment. It is not an exhaustive risk assessment of chemical additives but an exemplification of a methodology where known and reported additives representative for significant plastic types and product groups in Denmark are used. The risk approach elucidates the chain from product manufacturing to effects, via fate in the environment and uptake in organisms.

A pioneer study on flocculation of suspensions containing both natural sediment and microplastic (MP) particles has been carried out as part of the project and has shown significant flocculation and no fractionation of the MP particles compared to the other suspended particles. The result of the study is promising and there is a clear need for further studies using a combination of natural particles and MP particles in environmentally relevant concentrations.

The project has supported original research contributions, i.e. sedimentation of dolly ropes and the importance of MP flocculation, which has advanced the understanding and provided computer code that can be further developed and shared between researchers in the future. Both these studies have also given ideas about which aspects of bio-coating processes needs to be further investigated in the future.

To test the effects of potentially toxic MP particles in the marine environment, experiments were conducted where common coastal zooplankton species were exposed to increasing concentrations of new and old car tire particles and filling of artificial turfs (made from old tires), grained to be in a similar size range as the zooplankton prey. The results showed no increase in mortality or decrease in fecundity of zooplankton at or below 10,000 plastic particles per L, irrespective of the plastic type, zooplankton species or food level. As the concentrations of MP in Danish coastal waters are much lower, the short-term effects appear to be unlikely.

A discussion on analytical methods concludes that there is still no consensus on what techniques should be applied for sampling and analysis. A variety of different approaches have been taken, depending on the analytical equipment available, which makes it complicated to estimate field concentrations and to compare MP abundances and composition between areas and over time. Generally, μ FTIR is considered to be one of the most widely used methods for identifying MP accurately and quickly. However, there is a definite need to develop standardized methods for monitoring and also to formulate suitable indicators for defining the environmental effects of MP.

The problem of plastic particles of nano-size is also discussed, and finally it is discussed what data and knowledge is needed for improving the risk assessment of MP particles in the marine environment.

Risk Assessment

In collaboration with the plastic industry, seven cases of different polymer types that represent the most significant exposures of MPs and inherent chemicals and thus potential high-risk cases towards marine organisms or ecosystems, are defined. For each of these cases, product groups with significant use and release to the marine environment are identified:

- Low-density polyethylene (LDPE): Plastic bags, containers, bottles, tubing, personal care products and bud sticks.
- Styrene butadiene rubber (SBR): Car tires.
- Acrylate polymers (acrylics, polyacrylates): Paints for ships and pleasure boats.
- Polyvinyl chloride (PVC): Cables, cords, linoleum flooring also on ships.
- Polyurethane (PUR) rigid foam: Building insulation, construction material.
- Expanded polystyrene (EPS) foam: Building insulation and packaging.
- Polycarbonate (PC): Construction materials.

Numerous additives are added intentionally during manufacture including functional additives, such as flame-retardants, plasticizers and biocides. Other additive groups are colorants, fillers and reinforcements. Some additives have been used historically but have been banned, although older products and imported products may still comprise them.

Obtaining information and data on types and amounts of chemical additives used in plastics proved to be complicated. One reason is that all raw materials for Danish plastics converters are imported, and no manufacturing takes place in Denmark. Another significant explanation is lack of transparency due to confidentiality issues. Furthermore, additives are most often present in small amounts <1-2 wt-% and therefore it is not required to include them in safety data sheet for products. The data in this study are compiled from communication with the plastic industry, the scientific literature, manufacturers, reports and web sites.

Also during manufacture, some types of plastics may generate high contents of unreacted residual monomers and oligomers. Some monomers are classified as hazardous. For the considered cases the assessed residual contents are: 0.1wt-% ethylene (LDPE); 0.1wt-% 1,3-butadiene and 0.1wt-% styrene (SBR); 0.01wt-% acrylic acid (acrylic paint); 0.000001wt-% vinyl chloride (PVC); no residual monomers (PUR); 0.5wt-% styrene (EPS); 0.1wt-% bisphenol A (PC).

Risk associated to a given chemical on a MP is not only depending on the environmental concentration and toxicity of the chemical, but also on the specific polymer characteristics that has undergone weathering in the environment. In this study the toxicity of the polymers themselves is not considered, nor is the risk of chemicals sorbed from the surrounding environment (vector effect). For the risk assessment of residual additives, monomers and degradation products the risk assessment procedure for chemicals, outlined in the European Chemicals Agency (ECHA) guidelines that are based on the Technical Guidance Document, is used.

The risk towards marine organism in three trophic levels is calculated, i.e. pelagic/planktonic zooplankton: copepod (Copepoda), benthopelagic fish: atlantic cod (*Gadus morhua*) and seabird: northern fulmar (*Fulmarus glacialis*). For copepod, the exposure is via marine water, for cod via marine water or secondary poisoning and for fulmar via secondary poisoning as top predator

and direct ingestion of plastic particles at the sea surface. Predicted Exposure Concentrations (PEC) from maximum measured concentrations of MP in seawater and maximum measured or estimated micro and macro plastic amounts in the stomach/gut are:

- PEC (MP in marine water): 42 mgMP/m³
- Cod: 3.5 µgMP/kgbw/day and 700 µgMP/kgfood
- Fulmar: 1 gplastic/kgbw/day and 3430 µgplastic/kgprey

For Predicted No-Effect Concentrations (PNEC), Danish *miljøkvalitetskrav* (MKK) for other surface waters, according to BEK no 1625 of 19/12/2017, and European Environmental Quality Standard (EQS) values for other surface waters, according to Directive 2013/39/EU, for prioritized substances and certain other pollutants, are used. Additionally, EQS values for secondary poisoning derived in EU 2005 and 2011 dossiers, that form the basis of EU EQS values for prioritized substances in the water framework directive, have been used. In summary, MKK and EQS values for other surface waters are used as PNEC for the pelagic community in marine waters (copepod and cod), and EQS values for food intake (secondary poisoning) are used as PNEC for fulmar. When specific EQS values are available for food ingestion by fish these are used as PNEC, otherwise cod is assessed for the pelagic community.

Realizing the limited available data a fate and exposure scenario to describe the most significant processes and parameters is constructed. Maximum measured and estimated amounts of ingested macro and MP particles in the stomach/gut of fulmar and cod are used as exposure estimates. It is assumed that the ingested plastic consists of only one polymer type at a time. The amount of remaining monomer, additives and degradation products after weathering, i.e. corresponding to the ingested particles, is assumed to be 10 %. Solvents and volatile additives are assumed no longer present. A leachable fraction, estimated to 10% of the remaining chemicals represent the bioavailable fraction.

In the chosen fate-exposure-uptake scenario, some assumptions tend to be worst-case considerations, such as choice of one polymer at a time and use of maximum stomach content, where others have been adjusted to be more realistic, such as estimated leachable and bioavailable fractions.

Seventeen out of approximately 50 identified chemicals have MKK or EU-EQS values, and consequently also PNEC values, and thus they are included in the risk assessment. The risk quotients (RQ) defined as PEC/PNEC are therefore underestimated. The extent of underestimation is however not known. When more than one chemical is present, the RQs for individual chemicals are summed for copepod, cod and fulmar, respectively.

If there is a risk in these conservative scenarios, then more realistic scenarios, with more detailed process descriptions and data, need to be considered.

Potential risk, i.e. $RQ > 1$, is observed for the pelagic community (copepod and cod) and the flame-retardant pentabromdiphenylether (PeBDE) used in PUR, the biocide tributyltin (TBT) used in PVC and PUR, and the flame-retardant hexabromocyclododecan (HBCD) used in EPS. The highest estimated RQ for fulmar is 0.1 for PeBDE used in PUR.

Production of PeBDE in the EU ceased in 1997. The most common use, accounting for 95-98% of PeBDE since 1999, has been in PUR, which may contain between 10 and 18wt-% of the PeBDE formulation. The use of PeBDE was banned in the EU in 2004 through the Council directive 2003/11/EC relating to restrictions on the marketing and use of certain dangerous substances. Some recycling of articles containing these substances that were produced before introduction of the ban cannot be excluded.

Tributyltins can be present as impurities in mono- and dibutyltin stabilisers up to 1wt-%, but their content has voluntarily been controlled by industry to ≤ 0.67 wt-% (as tin). From July 2010 new products with >0.1 wt-% (as tin) are banned.

HBCD is listed in Annex A to the Stockholm Convention with specific exemption for production and use as flame-retardant in EPS and XPS in buildings until August 2017. After this date HBCD in EPS and XPS may still occur in the environment and furthermore significant amounts of HBCD is present in recycled PS packaging.

Another chemical with a relatively high RQ (0.1) for copepod and cod is the softener bis-(2-ethylhexyl)phthalate (DEHP) that is used in PVC.

For the remaining additives, i.e. metals and organic compounds, monomers and methylene dianiline (MDA) a degradation product from methylene di-phenyl diisocyanate (MDI) used in PUR, the estimated individual RQs and summed RQs are all below 0.08 indicating an additional margin of safety in relation to the conservative approaches used in this assessment.

This risk assessment of residues from intentionally added chemicals and degradation products in plastics is one of the first steps to unravel the potential risks from MP in the marine environment. Many issues still need to be investigated further in relation to production, fate, uptake and effects. Important data gaps are still not covered need to be covered, and important processes in the environment and the marine organisms should be investigated further. Recommendations for future work are therefore listed in the discussion section of the report.

1. Introduction

The occurrence of microplastics (MP) in the marine environment has been increasingly studied in the scientific community within the last decade (e.g. Avio et al., 2017). Most MP studies have so far focused primarily on MP, as a relatively uniform group, although not all types of MP particles are necessarily equally problematic to the environment. The polymer composition, addition of plastic additives, and the size and structure of the particles are likely to have a significant impact on the level of effects of MP particles in the marine ecosystem. In addition, physical processes can alter the harmful effects related to aging and weathering / dispersion of the microparticles (Tang et al., 2019).

It is estimated that plastic particles, which originate from car tires and paint flakes, are the dominant forms of MPs found in the Danish and Swedish aquatic environments (Lassen et al., 2015; Magnusson et al., 2016). Car tires and paint flakes can contain a variety of environmentally hazardous chemical substances, such as vulcanizing agents, biocides, heavy metals, etc. Similarly, there is a number of other types of plastic materials containing problematic chemistry, for example, foamed plastic with flame-retardants, as well as several types of plastic also contain different types of hormone disruptors. Further, besides the chemicals added during the production of the original plastic material, different plastic types might have the ability to absorb external hydrophobic substances (ECHA, 2019; Hansen et al., 2013; Lithner et al., 2011; Hahladakis et al., 2018).

A better understanding of the absorption processes for MPs and particular relevant chemical substances that may be associated with the plastic, and the resulting ecotoxicological effects in marine food chains will therefore be essential in order to conduct risk assessments for MPs in the marine environment. A number of environmental factors may affect the fate of MPs in the marine environment, i.e. what happens to MPs when they enter the ocean. Among other things, flocculation and aggregation of particles will be of great importance for both transport and sedimentation processes in the water column.

During the last decade, the studies on MPs have been increasing. Yet, a comprehensive knowledge is still missing on sources, occurrences, fate, effects and risks of various types of (micro) plastic. A knowledge that is needed for a better focus on research efforts, technology development as well as management measures. In addition, there is a considerable need for scientific knowledge on analysis methods to identify and quantify different types of MP in complex environmental samples, and, combined with analyses of environmentally harmful substances bound to the MP.

The aim of this report is to contribute with knowledge building on i) which types of MP and associated chemical additives that have the potentially highest risk towards marine organisms, ii) how to set up exposure scenarios for MP in the marine environment, iii) which analytical methods are best suited to detect and quantify MPs, iv) investigating the effects of selected MP in experimental investigations and v) investigating selected fate processes of MP in the marine environment. Such knowledge focusing on specific types of MPs will serve as a contribution to identify important product groups and to identify knowledge gaps that are necessary to investigate in order to improve the

risk assessment of MP and their associated chemical additives towards marine organism. The report builds largely on existing data from databases, scientific literature, plastic industry and expert knowledge and to a limited extent on newly generated data from experiments and model simulations. The results can benefit parties within the industry and environmental management on a local, regional and national scale as well as contribute to the rapidly growing research data portfolio on a national and international level.

2. Background and study results

2.1 Sources, emissions and occurrence of microplastics in the marine environment

Plastic pollution is recognized by the UN (UNEP 2016), the EU through the Marine Strategy Framework Directive (2008/56/EC) to achieve Good Environmental Status of EU marine waters by 2020 (EC, 2019), the Nordic council (Nordisk Miljøhåndlingsprogram 2019–2024), the Arctic council (AMAP), and national governments worldwide, as a serious threat to the marine environment. Up to 8 million tons of plastic waste is estimated to be discharged into the marine environment annually on a global scale; of these, 250,000 tons of plastic waste today circulate around the surface of the world's oceans. The discharge is expected to increase in the coming years (Eriksen et al. 2014; Jambeck et al. 2015).

Plastic litter and particles may be transported from global and regional sources with ocean currents, but may also originate from local emissions related to shipping, sea- and land based activities, dumpsites and sewage outlets. MPs may originate in the marine environment as primary or as secondary particles. Primary MP is produced industrially in the form of plastic based granulates or pellets which are used as microbeads in cosmetics, toothpaste, soaps etc. or as plastic pellets for industrial purposes. Secondary MP occurs through chemical and physical aging and degradation processes of macroplastic (e.g., plastic bags, plastic bottles, fishing nets or styrofoam products). As far as can be ascertained today, secondary MP is the main source of entry into the marine environment. The abundance of MP in the marine environment is typically expressed as number of particles per unit volume. In Table 1 a summary of MP abundance in Nordic and UK marine waters is made by Tamminga et al. (2018).

Table 1 Abundance of microplastic particles with location and sampling technique related lower detection limit. From Tamminga et al. (2018).

Country	Specific site	Abundance (per m ³)	Lower detection limit	Additional information
Denmark	North Sea	0.39	>100µm	No fibers included
Denmark	Kattegat	3.54	>100µm	No fibers included
Denmark	The Belt Sea	1.44	>100µm	No fibers included
Denmark	South Funen Archipelago	0.05-0.09	≥300µm	
Finland	Archipelago Sea	0.25	≥300µm	
Finland	Gulf of Finland	0.62	≥330µm	
Sweden	Stockholm Archipelago	0.19-7-73	>335µm	
Sweden	Göteborg harbour	0.9-2.9	≥330µm	WWTP adjacent
Sweden	Gullmarfjord	0.41	≥330µm	
Sweden	Kattegat	1.08	≥300µm	
Sweden	Stenungsund, Industrial harbour	Ca. 102550	>80µm	
Sweden	Skagerrak	7000-13000	>10µm	No fibers included
Sweden	Malmö, Industrial harbour	43.01	≥300µm	
Sweden	Ystad, inner harbour mouth	0.08	≥300µm	
Great Britain	Western English channel	0.27	≥500µm	
Great Britain	Northeast Atlantic	2.46	≥250µm	

2.2 Fate of microplastics in the marine environment

When entering the marine environment, the fate of the plastic is highly dependent on its density. Plastic materials such as expanded polystyrene (EPS) is highly buoyant and thus floats easily on the water surface where it is subjected to the influences of tide, wind, waves and ocean currents (Moore et al., 2001). As a result hereof, EPS is one of the major components of plastic debris on marine surfaces, and washed ashore on beaches globally, including the Baltic Sea (Strand et al., 2016; International Coastal Cleanup, 2017). Floating plastic material including EPS, will readily develop surface fouling covering the debris surface first with a biofilm followed by algal mat and then potentially also colonized by smaller invertebrates (Ye and Andrady 1991). For other types of plastic litter polyethylene (PET) and polypropylene (PP) with higher density than EPS, biofouling might at some level cause the density to exceed that of the seawater, facilitating that the plastic litter sinks in the water column and eventually deposits at the seafloor (Ye and Andrady 1991, Andrady et al., 2011).

When washed ashore, plastic fragments can still be very mobile by wind forces and they will therefore often accumulate in the upper part of the beaches or in the vegetation behind the beach or even further away (Strand, personal observations). The residence time of plastic fragments on beaches is therefore probably shorter compared to other more dense marine litter items deposited on the shorelines.

In the marine environment, plastic is fragmented due to different processes such as in general photodegradation, hydrolysis, mechanical degradation and thermal degradation besides biodegradation (Kubowicz et al., 2017) which creates increasingly smaller sizes resulting in the size fractions of microplastic and nanoplastics, see Table 2. While the degradation of plastic in the environment is considered extremely slow, the mechanisms and degradation times depend on the type of plastic, the content of additives and the area of deposition. During the fragmentation processes, chemical components such as polymer components such as styrene monomers, and chemical additives such as flame-retardants and plasticizers, can be leached to the environment due to larger surface areas formed by the continuous cracking (Kwon et al., 2017).

2.2.1 New study of microplastic settling to seabed

The fate of MP in coastal and marine environments is highly dependent on the settling velocity of the particles, i.e. the speed at which the particles settle to the bed. This in turn depends on the size and density of the particles. It is hypothesized that the transport dynamics of MP in many respects will resemble that of other inorganic particles. For the MP in the size range of sand and gravel (0.063 – 5 mm) this will involve transport, deposition and possible re-suspension of the MP as individual particles and the density of the polymer type will determine whether the particles will float or sink to the seabed. Biofouling, e.g. organic coatings with living microalgae, will typically increase the density and polymers, which are lighter than seawater, may therefore end up on the seabed anyhow.

MP in the size-range of clay and silt particles (smaller than 0.063 mm) are on the other hand likely to show significant interaction with other fine-grained suspended material and flocculation into aggregates with both organic and inorganic particles. The aggregates will be larger, mostly much larger, than their individual constituent particles whereas the density will depend on the

content of organic and inorganic particles, content of MP and the porosity of the aggregate. The relative concentration of MP compared to other suspended particles will vary across orders of magnitude but the concentration will be very low, even in highly polluted waters. The range of MP concentrations is still generally unknown but studies have reported values in the order of one MP particles to 1000 to 10,000 other suspended particles. Based on this it is assumed that clay- and silt-sized MP will interact and flocculate with other suspended particles and the settling velocity of MP will depend on the settling velocity of the aggregates, not on the size and density of the individual MP particles.

The flocculation and settling of fine-grained MP particles smaller than 0.02 mm have been examined in laboratory studies using both a camera set-up and settling chamber and in conventional settling tubes. The flocculation and settling of particles of SBR, acrylics and PVC have been examined as well as particles from low-density polypropylene. The main focus has been on PVC and our study shows that MP particles composed of PVC flocculated in both freshwater and seawater (Andersen, Skinnebach, Fruergaard, in prep). The particles also flocculate in control experiments but the aggregates get significantly smaller and settles at lower velocities. Larger and faster settling aggregates are formed in seawater than freshwater. The enhanced flocculation in natural fresh- and sea-water is ascribed to particulate and dissolved organic material, including both living cells and detritus.

A pioneer study on flocculation of suspensions containing both natural sediment and MP particles have been carried out as part of the project and has shown significant flocculation and no fractionation of the MP particles compared to the other suspended particles (Andersen et al., in prep).

2.3 Bioavailability and organism uptake

For plastic litter in general, entanglement and ingestion are the two mechanisms by which marine organisms are exposed to marine debris, with contamination from toxic compounds from the plastic material having sublethal effects on development and population dynamics as a secondary consequence (Wilcox et al., 2016). Especially plastic debris floating on surface waters or deposited on beaches and other coastal areas may be mistaken for food items by organisms and depending on the ingested amounts, the digestive system may clog, potentially leading to starvation and ultimately death. Ingestion of plastic particles in lower quantities may lead to malnutrition (Green et al., 2015; Jang et al., 2016). For example, studies have shown that stomach contents in seabirds like northern fulmars, shearwaters and albatrosses often contain meso- and micro-sized fragments of EPS among other plastic particles ingested (Moser & Lee, 1992; Rochman et al. 2016). These kinds of storm birds are species that mainly feed by finding food items floating on the water surface in the open oceans. As storm birds presumably cannot vomit, plastic particles can be contained in these birds for a long time. Plastic fragments in different size groups have also been found in other seabird species, in turtles (reviewed by Schuyler et al., 2013), whales and in oysters and mussels (Korrmann et al., 2015) among other species. Some organisms such as mussels may however also have the ability to excrete the particles ingested (Andrady, 2011). The size classes of plastic marine litter and the typical size of affected organism and application in industry are shown in Table 2.

Table 2 Size classes of plastic marine litter and typical size of affected organism and application in industry (Essel et al., 2015; Van Cauwenberghe et al., 2015; Andrady, 2017).

Diameter of plastic marine litter	Term	Typical size of affected organisms	Use in industrial applications
> 25 mm	Macroplastics	Vertebrates	Pre-products and end products
5mm – 25 mm	Mesoplastics	Birds, fish	Pre-products and granules (pellets)
1000µm – 5 mm	Large microplastic particles	Fish, crustaceans	Granules (pellets)
1µm – 1000µm	Small microplastic particles	Mussels, plankton	Microparticles in cosmetics
< 1µm	Nanoplastics		

The role of MPs as vectors for contaminant uptake has been discussed in scientific forums and papers. It is well known that organic chemicals in the surrounding environment can be sorbed by plastic including the associated biofilm. Various investigations regarding the different conditions of MPs present in marine and estuarine systems (e.g. salinity) (Bakir et al., 2014a; 2014b; 2016) or on the effect of the different characteristics of the polymers that constitutes them, are available (e.g. Andrady, 2011 & 2017; Graca et al., 2014; Rochman et al., 2013). When organisms ingest plastics with adsorbed contaminants, it is however heavily debated whether an increased bioavailability to organisms from this bidirectional interaction, i.e. sorption and release of chemical contaminants in plastics, can take place (Hartmann et al., 2017). In recent model analyses, it was reported that the effects of plastic waste on bioaccumulation of POPs may be rather small, due to a lack of a gradient between chemicals in plastic and the biota lipids, and that it is possible it can act as a cleaning mechanism for lipophilic substances with high Log K_{OW} values (Koelmans et al., 2014). Even though marine MP were found to have 100.000–1 million times higher concentrations of PCBs (polychlorinated biphenyls) and DDE (dichloro-diphenyl-dichloro-ethylene) than in the surrounding seawater (Mato et al., 2001) it is not known whether it serves as a significant increase in the load to the overall contribution. The hypothesis is also challenged with the argument that MP play a minor role in the environment compared to natural organic particulates and natural prey because of the relative lower abundance (Koelmans et al., 2016).

In the marine environment the behaviour for sorption/desorption of chemicals is related to plastic types, colour and other physical and chemical properties (i.e. size and chemical composition) of the MP besides the surrounding media. The sorption of chemicals to different types of plastic has for example been found to be LDPE ≈ HDPE ≥ PP > PVC ≈ PS (Wang et al., 2018), see Table 3 for abbreviations. Also, the effect of weathering/aging on plastic will enhance the sorption capacity of chemicals due to for example a higher specific surface area, the surface coverage of organic matter (Wang et al., 2018).

2.4 Effects and toxicity

In addition to findings of MP in organisms in field studies, effects of MP on marine species also need to be studied further. The harm of plastic fragments to marine organisms is mainly manifested in physical, but also chemical and biological effects.

At present, it is understood that polymers are, in general, not particularly reactive and their large size limits transport across biological membranes (Anastas et al, 2000). Therefore, polymers are often not considered hazardous in themselves (EC, 2012).

Various physical consequences from ingestion of plastic particles or entanglement of macroplastics have been reported and well documented for various species i.e. birds, turtles, fish larvae and marine mammals (Gregory, 2009; Steer et al., 2017; Jovanovic, 2017). Ingested debris may have specific effects on seabirds, such as physical damage and blocking of the digestive tract and impairment of foraging efficiency or even cause intestinal perforation, and ultimately starvation and death. The severity of these effects depends upon the types of debris ingested and their retention time within seabirds (Ryan, 1990).

Several studies performed in amphipods, lugworms, sea cucumbers, and mussels that have been exposed to MPs, have shown that these organisms tend to ingest the MPs as part of their natural feeding behaviour (Thompson et al., 2004; Browne et al., 2008; Steer et al., 2017). Further studies on the mussels demonstrated that the MPs were translocated from the gut to the circulatory system and were found in the hemocytes (Browne et al., 2008). Several consequences of exposure to MP in filter feeding organisms and deposit feeders are yet to be discovered (Hahladakis et al., 2018).

Ingestion of MPs have also been documented in a wide variety of plankton organisms, albeit typically at concentrations, which exceed many-fold the concentrations observed in the ocean (Botterell et al., 2018). Similarly, to the ingestion by larger organisms, the effects have mainly been connected to physical filling of the gut, and associated reduction in fitness due to malnutrition or starvation (Botterell et al., 2018).

With regard to chemical effects, there are three concerns; the vector effect, additives intentionally added to the plastic during manufacture or processing and residual monomers in the plastics. As mentioned previously the vector effect whereby organic contaminants present in seawater sorb to MPs and in this way is taken up by the organism under natural environmental conditions, is being debated. The potential effect from ingestion of contaminated MPs depends on the bioavailability of the organic contaminants, the body mass of ingesting organism, the concentration of contaminants in or at the MPs, the modification of the surface of the plastic due to weathering and their propensity to bioaccumulate in the organism (Andrady 2017; Peng et al., 2017). Additives are manifold and include stabilizers, plasticizers and flame-retardants added intentionally during manufacture. These chemicals may be found at relative high concentrations (10-15wt-%) and potentially become bioavailable after ingesting by organisms (Andrady 2017).

Also during manufacture, some types of plastics may have high contents of unreacted residual monomers and oligomers, such as vinylchloride and polystyrene (Peng et al., 2017). For polystyrene, this fraction may be as high as 0.6 wt-%. Some monomers are classified as hazardous. For example, polyurethane foam, PVC, polycarbonate and high-impact polystyrene, are composed of monomers that are considered carcinogenic, mutagenic or toxic for reproduction (Lithner et al. 2011). Other monomers that have been described as the most environmentally hazardous are m-phenylenediamine, p-phenylenediamine, 1,4-dichlorobenzene and the plasticizer butylbenzylphthalate (BBP) (used as a monomer in some PVC), all of which have been found to be acutely toxic to aquatic life (Lithner et al. 2011). Biological effects in the ingesting organisms may be related to the increased intake of microorganisms adhered to the MPs or introduction of new or non-native species into other areas through transport of plastic debris by ocean currents and winds (Andrady, 2017; Wang et al., 2018).

Fragmentation of plastic fragments may also lead to nanoparticles. Due to their small size in nature, nanoplastics may cross cell membranes and thus penetrate tissues and accumulate in organs (Koelmans et al., 2015; Mattsson et al., 2015). Apart from the physiological consequences, nanoplastics may also have toxic effects (Koelmans et al. 2015). The high surface area may cause strong sorption affinity for chemical compounds leading to toxicity once the nanoparticles have passed the cell membranes. The environmental impacts of nanoplastics may thus be different and pose other risks than those of MPs.

2.4.1 New study of car tires and zooplankton

The current project enabled a possibility to test the effects of potentially toxic MP particles in marine environment. New conducted experiments were set up by exposing common coastal zooplankton species to increasing concentrations of new and old car tire particles and filling of artificial turfs (made from old tires), grained to be in a similar size range as the zooplankton prey (Koski et al., in prep). Besides quantifying the effects of toxic MP, it was investigated how various factors influenced the response of zooplankton to plastic – particularly since literature studies report both effects and no-effects of MP on plankton organisms (Botterell et al. 2018). It was expected that the factors which could add variation to the response of organism could be related to the properties of plastic particles (concentration, toxicity), properties of the plankton species or populations (feeding mode, physiology) or to the environment (food concentration). The results showed no increase in mortality or decrease in fecundity of zoo-plankton at or below 10,000 plastic particles per L, irrespective of the plastic type, zooplankton species or food level (Figure 1a). As the concentrations of MP in Danish coastal waters are several orders of magnitude lower (e.g., Beer et al. 2018), see Table 1, short-term effects appear to be very unlikely since the margin of safety between realistic exposure and observed acute effects are at least 1,000,000 in open sea. For sublethal effects from long-term exposure this margin may be lower, see Figure 1. Furthermore, in areas that are heavily polluted with floating MP particles, such as coastal waters, harbours or narrow straits with e.g. up to 100,000 particles/m³ adverse effects can potentially occur, see Chapter 3.

The feeding and pellet production (combined measure of feeding and assimilation) of zooplankton were influenced by concentration and type of MP, food level and zooplankton species (Figure 1b). In short, these interactions suggested that zooplankton species which create a feeding current are more vulnerable for plastic pollution than species which feed more selectively on single particles, that the effects are stronger at low food concentration, and that while less-toxic particles (old tires) typically increase pellet production due to their physical effect on gut fullness, more toxic particles (new tires) have an inhibitory effect. The results thus indicated complex interactions of plastic properties, abiotic factors and plankton communities, which need to be taken into account when estimating the effects of MP pollution in the marine environment.

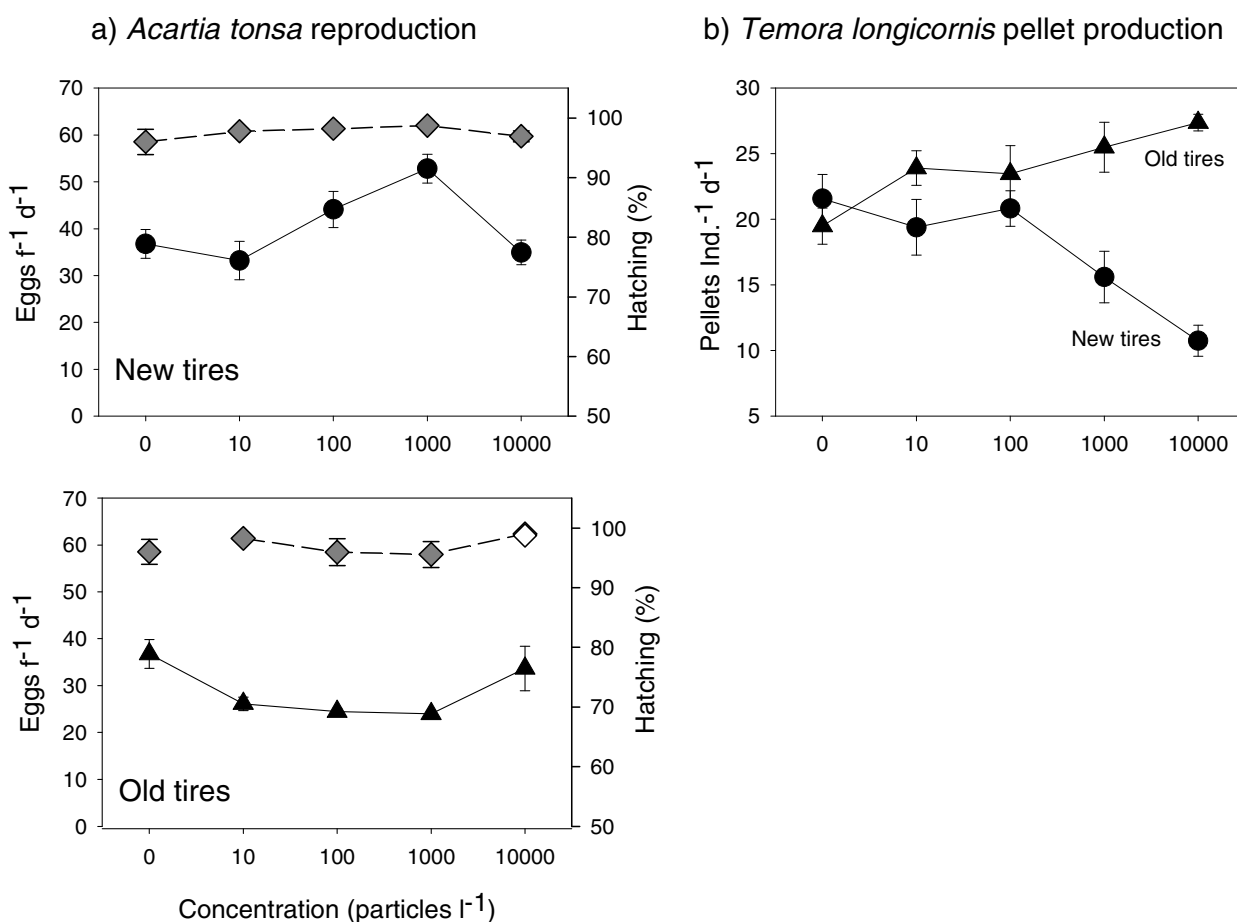


Figure 1a and 1b Reproduction and pellet production of common coastal zooplankton species exposed to increasing concentrations of new and old car tire particles and filling of artificial turfs (made from old tires), grained to be in a similar size range as the zooplankton prey (Koski et al., in prep.).

2.5 Monomers and polymers

A polymer is a substance consisting of molecules characterised by the sequence of one or more types of monomer unit. Such molecules must be distributed over a range of molecular weights. Differences in the molecular weight are primarily attributable to differences in the number of monomer units. A polymer is defined as a substance meeting the following criteria: i) Over 50 percent of the weight for that substance consists of polymer molecules, ii) The amount of polymer molecules presenting the same molecular weight must be less than 50 weight percent of the substance (ECHA, 2012).

Polymers are made by polymerising monomers into macromolecular chains and are incorporated into a plastic compound with different additives. Additives are chemical compounds added to improve the performance (e.g. during shaping of the polymer, through injection moulding, extrusion, blow moulding, vacuum moulding, etc.), functionality and ageing properties of the polymer. Each of them plays a distinct role in delivering/enhancing the functional properties of a plastic product. Additives can be divided into the following four main categories: i) Functional additives (stabilisers, antistatic agents, antioxidants, flame-retardants, plasticizers, lubricants, slip agents, curing agents, foaming agents, biocides, etc.), ii) Colorants (pigments, soluble azo-colorants, etc.), iii) Fillers (mica, talc, kaolin, clay, calcium carbonate, barium sulphate), and iv) Reinforcements (e.g. glass fibres, carbon fibres). Additives are, most often, not chemically bound to the plastic polymer. Only the reactive

organic additives, e.g. some flame-retardants, are polymerised with the plastic molecules and are becoming part of the polymer chain. (Hahladakis et al., 2018; EC, 2012).

Databases such as ECHA (2019), SpecialChem, BASF, AccuStandard (2013), Flick (2004), Harper & Petrie (2003) and Zweifel et al. (2009) have registered several thousand polymer additives. Some have trade names that have confidential chemical constituents.

Polymerisation reactions are rarely 100 % complete and, thus, unreacted monomers and in some cases reaction by-products may be found in the polymer. The proportion of unreacted monomers or by-products, can vary greatly depending on type of polymer, polymerisation technique and techniques for reducing the levels of these constituents. In a review by Araújo et al. (2002), the proportion of unreacted monomers or by-products varied from no or very low levels (100 ppm; i.e. 0.0001wt-%) to up to 40,000 ppm (i.e. 4wt-%).

However, industry carefully controls polymerisation to ensure that the resultant polymer has the desired properties. The minimisation of residual monomer content is also often a priority as residual monomers can result in increased hazards while representing decreased production efficiency and increased costs. For example, great efforts are made to minimise the residual vinyl chloride monomer (VCM) content in polyvinyl chloride (PVC). The OECD SIDS programme identified VCM concentrations in final PVC products to be (OECD, 2001) <1 ppm residual VCM in PVC products, in 1991 with data suggesting that by 1998 figures were a factor of 10 lower; and <10 ppb VCM in modern medical grade PVC (in 1992).

Other polymerization impurities that can be present in a polymer are oligomers, low molecular weight polymer fragments, catalyst remnants and polymerisation solvents, as well as a wide range of plastic additives including processing aids and end-product additives (Crompton, 2007). All these components are usually of low molecular weight and therefore, may, migrate from a plastic product or finished article (Crompton, 2007) to air, water or other contact media (EC, 2012).

Plastic polymers exhibit varying physical/chemical properties that influence their environmental fate. Hydrophobicity (polarity) determines their function in products, affinity to chemicals, and behaviour in the environment and inside organisms. Polymers with the highest global and European plastic demand (EC, 2012) and polymers that are relevant for products related to the marine environment are stated in Table 3 together with common monomers and polymer polarity. Application in products that are relevant for the marine environment are addressed in the following sections.

Table 3 Hydrophobicity (polarity) and common monomers.

Polymer	Common monomer (CAS no) (EC, 2012)	Polarity
Polypropylene (PP)	Propene (115-07-1)	Non-polar
Low-density polyethylene (LDPE)	Ethylene (74-85-1)	Non-polar
High-density polyethylene (HDPE)	Ethylene (74-85-1)	Non-polar
Polystyrene (PS)	Styrene (100-42-5)	Non-polar
Acrylic polymers include the acrylates, polyacrylates	Acrylamide (79-06-1), Acrylic acid (79-10-7), Methacrylic acid (79-41-4), Acrylonitrile (107-13-1), Methyl Methacrylate (80-62-6), 2-Ethylhexylacrylate (103-11-7), Methyl acrylate (96-33-3), Ethyl acrylate (140-88-5), Butyl acrylate (141-32-2), Trimethylolpropane triacrylate (TMPTA) (15625-89-5), Vinyl chloride (75-01-4)	Non-polar
Polymethyl methacrylate (PMMA) (Plexiglas)	Methyl Methacrylate (MMA) (80-62-6)	Polar
Polycarbonate (PC)	Diphenyl Carbonate (102-09-0), Bisphenol A (80-05-7), Phosgene (75-44-5)	Polar
Polyurethane (PUR)	4-methyl-mphenylene diisocyanate (TDI) (584-84-9), 4,4'-methylenediphenyl diisocyanate (MDI) (101-68-8), Diphenylmethane-diisocyanate, isomers and homologues (9016-87-9), D-glucitol (50-70-4), Ethylene oxide (75-21-8), Methyloxirane (75-56-9)	Polar
Polyamide (PA) (nylon)	11-aminoundecanoic acid (2432-99-7), Adipic acid (124-04-9), ϵ -caprolactam (105-60-2), Dodecane-12-lactam (947-04-6), Hexamethylene-diamine (124-09-4)	Polar
Polyethylene terephthalate (PET) (Dacron)	Terephthalic acid (100-21-0), Dimethyl Terephthalate (120-61-6), Ethane-1,2-diol (107-21-1)	Polar
Polyvinyl chloride (PVC)	Vinyl chloride (75-01-4)	Polar
Epoxy resins	1-chloro-2,3-Epoxypropane (106-89-8), Bisphenol A (80-05-7), Cyanoguanidine (461-58-5), Dapsone (80-08-0)	Polar
Polytetrafluoroethylene (PTFE) (Teflon)	Tetrafluoroethylene (116-14-3)	Non-polar
Acrylonitrile-butadiene-styrene (ABS) terpolymer	Acrylonitrile (107-13-1), 1,3-butadiene (106-99-0), Styrene (100-42-5)	Polar
Styrene-butadiene rubber (SBR)	1,3-butadiene (106-99-0), Styrene (100-42-5)	Non-polar

2.6 Nanoplastics/-particles

As mentioned plastics will degrade from micro-size fragments to nano-size fragments in the environment due to ageing and weathering. The time needed for this degradation is obviously dependent on the plastic type and the additives, i.e. chemicals/materials that are embedded. As the fragments become smaller, there is an increasing surface-to-volume ratio and release of the embedded materials/compounds from the plastics (Scott-Fordsmand et al. 2017). Hence, as the plastics weather to the nano-size there are a variety of concerns associated with the nano-sized pure plastic fragments, with the nano-sized plastic fragments that contain embedded materials/compounds, and with the nanomaterials/compounds released from the plastic. These fragments will differ in size, shape and surface characteristics, parameters that will affect the fate, exposure and hazard (e.g. Gomes et al. 2018). The risk associated with

such nanoscale-materials and -fragments is understood much less than risk associated with conventional chemicals (Scott-Fordsmand et al. 2016).

There has been some emphasis on the risk from nano-sized plastic fragments, and much less on the risk from nanomaterials leaching as the polymer degrades (Scott-Fordsmand et al. 2017). This is the case for the aquatic environment, but even more noteworthy for the terrestrial ecosystems, where most of the plastics are deposited and degrade (MST 2015, 2017). Previous risk related research in the nanoscale has mainly focussed on the potential risk of pristine nanomaterials (including polymer-based materials) showing that toxicity is related to a variety of factors, e.g. inherent material properties, shape/size, and surface characteristics (Carnovale et al. 2016). In general, uptake into cells is inversely size related and occurs mainly below 1 μm . However, it is not trivial to estimate the risk related to nano-sized materials/-fragments. This is, among other things, because it is difficult to obtain representative reference materials (i.e. not only representing the pristine state), it is difficult to quantitatively identify nano-sized materials in complex media, and most of the current hazard test systems are not designed or optimised for nanomaterial testing (Hund-Rinke et al. 2016, Amorim et al. 2018). For example, a reoccurring problem in hazard testing is the influence of nanomaterial related phenomena, e.g. gravitational, random movements and agglomeration that all influence the behaviour and toxicity of the nano-fragments. This makes well-characterised, homogenous and repeatable experiments very difficult (Scott-Fordsmand et al. 2017). Further, the nano-fragments and nanomaterials released from the plastics cannot be assumed to be similar to the original plastic or to the originally added nanomaterials. Moreover, there is no indication that the released nanomaterials in general are less toxic than the parent (pristine) nanomaterial.

Hence, to get a sufficient understanding of risk, studies must be conducted with materials identical or similar to the nano-sized fragments and to what is leached from the plastic. This means longer-term experiments should be conducted (e.g. Gonçalves et al. 2017) with weathered plastic fragments, in which nanomaterials are embedded. It is important that the fragments are allowed to weather fully in the test-systems in order to mimic what happens in the environment. If weathering is omitted, the experiment may fail to show biological effect, even in cases where a biological effect would be present in the longer term under realistic conditions. For example, biological experiments often start with large fragments (e.g. larger than 100 nm), because it is difficult to obtain homogenous samples of smaller fragments, and the test duration (e.g. 28 days) does not allow most polymers to be degraded sufficiently to release embedded material. Such experiments cannot conclude on the potential for long-term effects even if effects were absent. The way forward is to develop suitable analytic techniques for complex environments (although this may take a long time) to develop long-term hazard tests that can include the long-term degradation of the plastics. This should cover all life cycles of the materials.

2.7 Overview of analytical detection methods

There is still no consensus on what techniques should be applied for sampling and analysis of MP and nanoplastics. A variety of different approaches has been taken, which make it complicated to estimate field concentrations and to compare MP abundances and composition between areas and over time. The methods used will depend on the analytical equipment available. This can

range from simple visual identification using a stereo microscope to more advanced infrared mapping techniques such as Focal Plane Array (FPA) based μ Fourier Transform Infrared Spectroscopy (FTIR). These methods will differ in the time it takes to analyze samples as well as the specific information that is gathered about the MP. Hence, there is a definite need to develop standardized methods for monitoring and also to formulate indicators for defining the environmental effects they have.

μ FTIR is one of the most widely used methods for identifying MP accurately and quickly, see Figure 2. FTIR spectra can be compared to a reference library of spectra. These comparisons are usually done by conducting a correlation with reference spectra giving a similarity index based on how well it matches with the sample spectra. There is no single method that is suitable for identification of all MP particles, however, FTIR is the recommended method and the most widely used method for the identification of MPs (Shim et al., 2017). Advances in FTIR technology has meant that the traditional method of analyzing samples particle by particle after visual identification can now be reduced or avoided entirely. FPA based μ FTIR allows for the analysis of large numbers of particles producing thousands of spectra in a single scan. This means that many particles can be analyzed at once. Spectra from a particle of interest can then be selected and put through a library search to identify them.

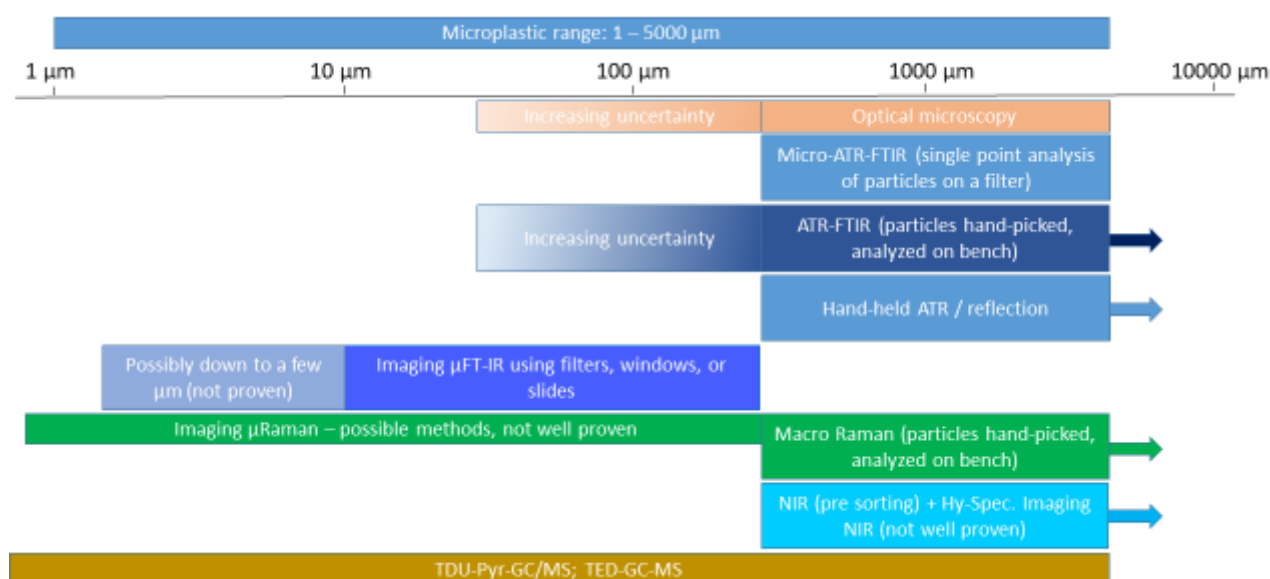


Figure 2 Analytical methods suitable for microplastic detection – size ranges vs analytical method.

MPhunter is a program developed in Aalborg University in collaboration with Alfred Wenger Institute that is specifically designed to automate large amounts of the analysis in order to identify MP particles. The reference library used can be adjusted to improve the accuracy of the automated detection. If a new polymer is found that is not part of the library it can be selected in the software and added to the search.

The accuracy of the automated identification of particles will be dependent on the quality of the spectral library used as well as the threshold that are set for individual spectra. Due to the samples presence in different compartments of the environment there could be some fouling of the MP. There is therefore a certain level of subjective interpretation based upon experience and expertise

of the individual analyzing the spectra, which is required to accurately identify the particles (Renner et al., 2018).

Before analysis, the sample must be pre-treated and concentrated according to the type of sample and the used instrumentation. This can for example include pre-sieving through a 2mm mesh to remove larger components, pre-oxidation with H_2O_2 , enzymatic removal of organic matter, Fenton oxidation, filtration through 10 μm steel filter, sonication in ZnCl_2 , flotation in ZnCl_2 , filtering through 10 μm steel filter, filter sonication in EtOH and adjustment of volume.

3. Risk assessment of different types of plastic polymers

As concluded by Syberg et al. (2015) evidence-based decision-making with respect to ecological exposure to MP as well as effects and derived risks posed by MP, are in fact what science is lacking.

An essential step towards making a risk assessment is a hazard assessment where the inherent toxicity of a chemical is assessed. Lithner et al. (2011) made a ranking of plastic polymer types based on hazard classifications of monomers and a hazard ranking of monomers and their presence in polymers using the harmonized hazard classifications assigned by ECHA under the European Classification, Labelling and Packaging (CLP) legislation (EU, 2008). Harmonized CLP classifications (hazard category and class) were extracted from the ECHA-provided file “Annex VI to CLP_ATP10”. Groh et al. (2019) used an extended version of this approach to make a hazard assessment based on selected harmonized hazard data and compiled a database of chemicals associated with plastic packaging, which includes chemicals used during manufacturing and/or present in final packaging articles. The database lists 906 chemicals likely associated with plastic packaging and 3377 substances that are possibly associated.

The next step from a hazard assessment is estimating the exposure and calculating the corresponding risk quotient. The actual risks to the environment remain highly uncertain. Perceived impacts of plastic debris are mainly based on evidence of the presence of plastic, which often is framed as “huge” or “ubiquitous” without taking into account the threshold concentration above which an effect occurs, or at least acknowledging that the actual risk is in fact indeterminate as long as environmentally realistic exposure concentrations are not compared to the effect thresholds (Koelmans et al., 2017). For exposure assessments to be useful for risk assessment purposes, the quantification of MP should be specified with regard to volume of the specific water body. It is essential to know the type, size and number of MP per unit volume of water taken in by these organisms to answer how exposure varies through space and time. Many studies simply have been presence-absence measures based on tows, without determination of the number of MP per volume of water. This does not allow for quantitative determinations of organism exposure, which would likely be by feeding (Syberg et al., 2015).

The existing framework for ecological risk assessment, which is used in regulatory contexts for chemicals worldwide, is yet to be applied to marine MP. Therefore, it is not possible to univocally demonstrate whether MP contamination poses a risk to the marine environment.

Everaert et al. (2018) performed an ecological risk assessment of marine MP pollution for marine biota and their ecosystems, based on available data, by calculating the current exposure of marine systems to MP in combination with an effect assessment to quantify the safe environmental concentration of MP. The study's primary focus was at the direct effects of MP exposure, and not the indirect effects associated with the chemicals present in and on MP. Based on historical annual total plastic production figures of 1950 to 2016 and a projected annual global growth of 4.5 % in plastics production between 2017 and

2100 the past and future concentrations of pelagic free floating MP concentrations, from <1 mm to 5 mm, were calculated to be 0.2-0.9 particles/m³ in 2010, and 9.6-48.8 particles/m³ in 2100, for a best and worst case scenario, respectively. For all model assumptions, see Everaert et al. (2018).

Comparing these predicted environmental concentrations with in situ observations revealed that the predicted MP concentrations were within the range of in situ MP concentrations, but did not span the entire range of the observed concentrations.

For the effect assessment, they scanned the available scientific literature for effect data that expose marine organisms to MP, resulting in a predicted no effect concentration (PNEC_{pelagic}) of 6650 particles/m³. The risk assessment thus revealed that no imminent threat of MP pollution up to 2100. However, in areas that are heavily polluted with floating MP particles, such as for example in coastal waters (>100,000 particles/m³) or in narrow straits such as the Queen Charlotte Sound in the NE Pacific Ocean (9200 particles/m³) adverse effects can potentially occur.

3.1 Setting the frame for risk assessment of micro plastic in the marine environment

Developing a rational risk assessment framework for MP comes with several challenges. For instance, the metric used to quantify the effect should be ecologically relevant and should be the same as the one used to quantify exposure. For conventional chemicals, this ecologically relevant metric is the concentration (Koelmans et al., 2017).

For a MP source, there are basically three parameters, determining the risk that can be varied in multiple ways; plastic polymer type, chemical additives and product/activity. Existing data on environmental occurrence are usually based on only chemical (where plastic type is not defined) or only on plastic type, and in some cases on both chemical and plastic type.

However, risk is not only depending on the environmental concentration and toxicity of a chemical on any MP. A realistic risk assessment should be for the chemicals on a MP with specific polymer characteristics. This chemical-MP complex should be assessed with respect to use, emissions, environmental fate, environmental occurrence, uptake and effects in marine organisms, as illustrated in Figure 3.

ECHA (2019) lists a combined set of characteristics that have drawn the attention of ecotoxicologists to their safety and toxicity:

- Persistence i.e. resistance to (bio)degradation
- Increasing input to the environment – corresponding to the increased use of plastics worldwide
- Potential to cause harm to organisms via direct and indirect mechanisms
- The presence of chemical contaminants within and adsorbed to the plastics that are known to cause harmful effects
- Limited potential for removal (i.e. remediation) once in the environment

In this report, risk estimates based on the exposure and toxicity of the chemical additives towards marine organisms, are calculated. MP as vectors for sorption of environmental chemicals is not considered. Moreover, the effects

of polymers themselves, apart from residuals of the monomer building blocks, are considered.

The common approach is that the amount of remaining additives and residuals are negligible, either because the added concentrations in the plastic are very low, below 1-2 %, or simply because the added compounds and amounts are not known. Furthermore, a quantitative estimate of remaining chemicals and their bioavailability after weathering is not known for the many plastics of interest. Nevertheless, a methodology is set-up for selected cases of plastic polymers, and it is illustrated how available data can be used. It will not be a complete risk assessment covering all additives present in MP in the marine environment but it will highlight available data and process knowledge as well as identifying data gaps.

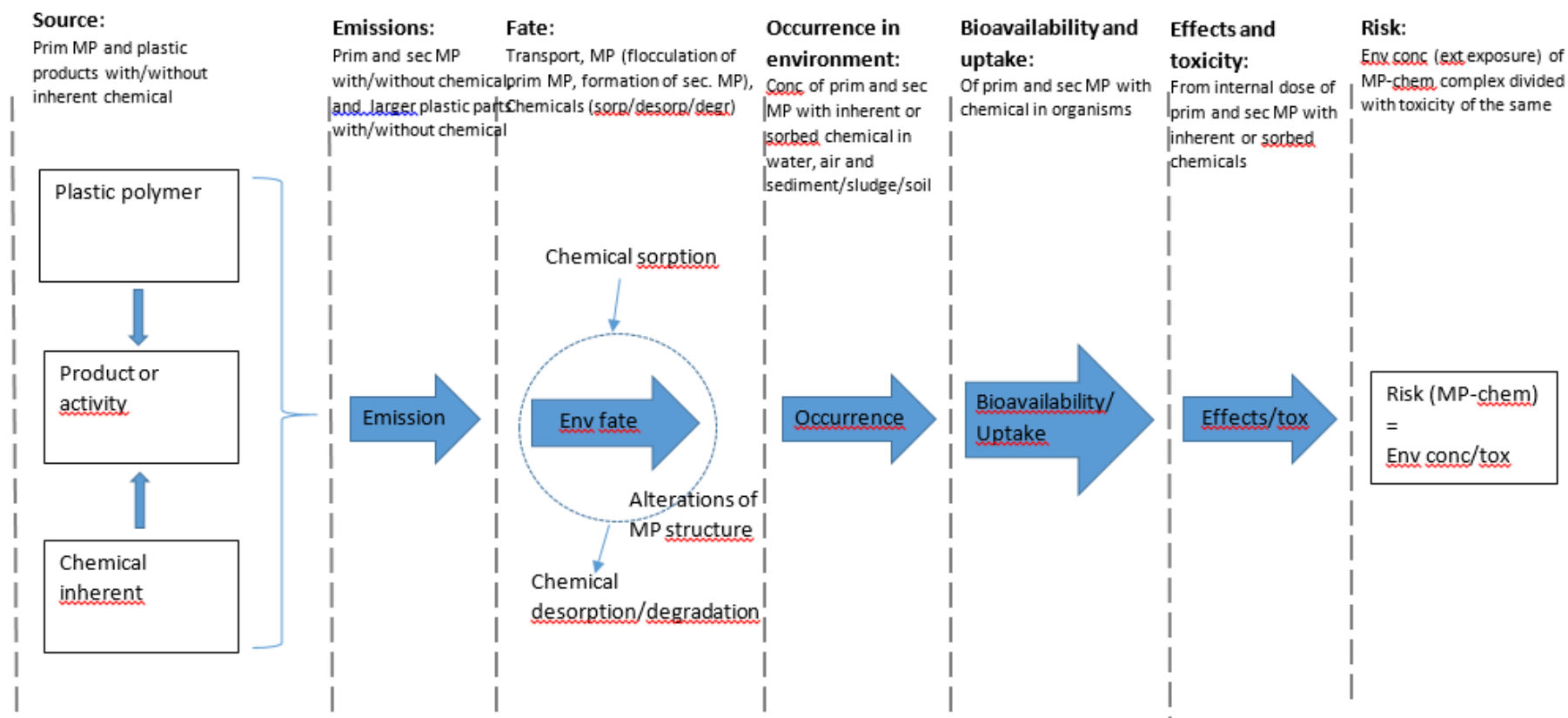


Figure 3 Risk assessment of MP-chemical complex: Frame for assessing source to risk of MPs in the marine environment.

In Figure 3, the different elements in assessing the marine risk of MPs are outlined. They comprise:

- Sources, i.e. description of polymer type, inherent chemicals and their use in consumer and industrial products and industrial applications. Data needs: Amounts of used polymers, inherent chemicals, and products.
- Emissions data from sources – and challenges with developments of good quantitative measurements for MP. This comprises emissions of primary and secondary MP with and without inherent chemicals. Also of relevance are emissions of larger plastic parts with and without chemicals that eventually can become MP in the environment. Data needs: Emission factors to surface waters and marine waters, sewage and air, for products and polymers.
- Environmental fate incl. transport, weathering, flocculation of primary MP, formation of secondary MP, sorption/leaching/degradation of inherent and environmental chemicals. Data needs: Physical/chemical properties of polymers and inherent chemicals, e.g. hydrophobicity and volatility, and relevant process parameters, degradation rates. Systemic needs: Modelling of fate processes.
- Occurrence and distribution in the different environmental compartments. Data needs: Quantitative measurements of polymer compositions in micro- and macroplastic, and their associated chemicals, in the environment. Systemic needs: Modelling of occurrence, e.g. describing point sources vs coastal waters vs. open waters.
- Bioavailability and uptake includes uptake- and elimination rates of chemicals depending on routes of exposure from/to water, food and plastic. Chemical leaching in organism of sorbed contaminants from virgin vs. aged MP, considering particle sizes and shapes. Data needs: Distribution coefficients and desorption rates under varying gut conditions (different pH and temperature scenarios). Systemic needs: i) Gut retention time of ingested particles, ii) physiological processes such as the presence of enzymes or gut surfactants and iii) differing physiological conditions of pH and temperature according to the type of organism. Understanding the roles of iv) dilution of internal chemical concentration by sorption to MPs, v) increased internal chemical concentration by ingestion of MP (carrier) with inherent chemicals, and vi) decreased internal chemical concentration by ingestion of clean MP with the potential of chemical sorption.
- Toxic effects. Data needs: Toxicity parameters for polymers, and toxicity parameters for inherent chemicals. Systemic needs: linking exposure/uptake to both subchronic effects and more population relevant endpoints. Furthermore, the potentially increased risk from nanoplastics.
- Risk: Combining occurrence, internal exposure and toxicity measures. Systemic needs: description and application of more realistic exposure and uptake scenarios.

3.2 Risk assessment procedure in this report

The risk assessment procedure in this report is based on the Technical Guidance Document (EC, 2003) as outlined in the Guidelines of the European Chemicals Agency (ECHA). The guidance is a framework consisting of an initial information gathering (hazard identification) followed by an exposure assessment, based on the R.16 guideline (ECHA, 2016), and a hazard assessment, based on the R.10 guideline (ECHA, 2008), leading up to the risk characterization. In short the outcome is a predicted environmental concentration (PEC), a predicted no effect concentration (PNEC), and a risk quotient (RQ).

The risk assessment is based on the predicted amount of chemicals in the predicted amount of MP types. It comprises priority substances in the Water Framework Directive and certain other substances as listed in BEK 1625 and Directive 2013/39/EU.

The following (groups of) species are included in the assessment: Pelagic/planktonic zooplankton: copepod (*Copepoda*); Benthopelagic fish: atlantic cod (*Gadus morhua*); Seabird: Northern fulmar (*Fulmarus glacialis*). The choice of species in different trophic levels is analogous to the study by Bakir et al. (2016) that examined the potential for plastics to act as a vector in the transport of hydrophobic organic chemicals from seawater to marine organisms.

3.2.1 Predicted Environmental Concentration (PEC)

The exposure concentrations of plastic additives, monomers and degradation products are derived from maximum measured concentrations of MP in seawater and from maximum measured or estimated micro and macro plastic amounts in the stomach/gut of the organisms.

For copepod, the exposure is via marine water, for cod via marine water or secondary poisoning and for fulmar via secondary poisoning as top predator and direct ingestion of plastic particles at the sea surface. For cod and fulmar, measured or estimated micro and macro plastic amounts in the stomach/gut are used as a measure for the total exposure of plastic.

Concentration of MP in bulk water: The concentration of MP in the water column is varying according to sampling site and lower limit of detection. When performing in situ measurements only particles larger than the mesh size are retained. Hence, the smallest MP slip through the mesh of the nets and are thus not counted. Those small particles have a large contribution in the total mass and in the total number of MP particles expressed per volumetric unit. Everaert et al. (2018) states that the mean concentrations when using a mesh size of 50 mm were two orders of magnitude greater than when using a sampling net of 330 mm, and 100,000 times more MP was collected with an 80-mm mesh net than with a 450-mm mesh net.

From Table 1 and background data in Everaert et al. (2018), a high MP concentration most representative of the entire range of MP, i.e. 1µm to 5mm can be set to approximately 10.000 particles/m³ = 10 particles/L. Assuming these are spherical with a diameter of 100 µm and specific gravity of 1 the concentration in mass is **42 mgMP/m³**.

Ingested amounts: *Fulmars* forage near the water surface at sea and never on land, and the ingested amount of micro and macro plastic particles found in their stomachs are assumed to originate from plastic litter/particles floating at the sea surface. These may contain items from deeper water, and items that may be ingested through their prey. Fulmars normally do not regurgitate the fraction of hard remains from the prey. Indigestible food parts accumulate in the muscular part of the stomach to be slowly ground mechanically down to a size that may pass into the gut. Plastic particles can reside in fulmar stomachs for several months. Consequently, the abundance of hard prey remains in the stomach, including plastics, provides an integrated representation of items ingested over a period of time before death (Hertzke et al., 2016; van Franeker et al., 2011).

Maximum amount of micro/macro plastic measured in the stomach in a single dead fulmar were over 20 g and over 1600 pieces (van Franeker et al., 2005). This amount can be compared to the OSPAR Ecological Quality Objective (EcoQO) limit value of 0.1 g per bird, which is a target value for 'acceptable ecological quality' defined by OSPAR as the situation where less than 10 % of fulmars carry more than 0.1 g of plastic (OSPAR, 2008).

Barrett et al. (2002) found from an average body mass of 810 g, and a consumption of 31,624 metric tonnes of prey per year, an average "normal prey" ingestion rate of 0.3 gprey/gbody weight (bw)/day. Hertzke et al. (2016) calculated an ingestion rate for plastic, assuming that the accumulation of plastic in the fulmars' stomach is a balance of accumulation and loss processes using a 1st order removal rate constant from the stomach of 0.0462 d⁻¹. This was estimated by Van Franeker et al. (2011) from a loss rate of 75 % of ingested plastic in one month. At steady state, the ingestion rate for plastic was calculated from the product of a measured average concentration of plastic in the fulmars stomach (0.3 gplastic/973 gbw = 3.083E-04 gplastic/gbw) and the first order removal rate constant, to be 3.083E-04 gplastic/gbw * 0.0462 d⁻¹ = 1.43E-05 gplastic/gbw/day. The fraction of plastic in the ingested food was calculated as 1.43E-05 gplastic/gbw/day / 0.3 gprey/gbw/day = 4.75E-05 gplastic/gprey. This indicates that ingestion of plastic mass is negligible compared to the mass of ingested prey per unit of time.

Using the maximum measured plastic amount of 20 g per 900 gbw (approx.) = 2.22E-02 gplastic/gbw, an ingestion rate for plastic is 2.22E-02 gplastic/gbw * 0.0462 d⁻¹ = **1 gplastic/kgbw/day**, and a fraction of ingested plastic in ingested food to be 1.03E-03 gplastic/gbw/day / 0.3 gprey/gbw/day = **3430 µgplastic/kgprey**.

Cod: Cod can be found at depths ranging from very shallow coastal areas and down to 600 m. Cod are considered benthopelagic demersal fish, i.e. living and feeding near the bottom as well as in midwaters. They feed on both benthic as well as pelagic organisms (Lenz et al., 2016). Cod is known to ingest a whole range of prey from plankton, shrimps and crayfish to fish including its own species, which makes them prone to ingesting anthropogenic matter from both pelagic and benthic habitats.

Bråte et al. (2016) found in 302 cod samples along the Norwegian coast that all, except one, of the stomachs that contained plastic (n = 9), were full of organic content (n = 202), suggesting a plastic gut clearance rate similar to the ingested food. They proposed that stomach fullness is an important metric in order to avoid underestimations when assessing the levels of MP ingested by fish. Limitations in such studies are identifying MP smaller than approx. 2 mm, and distinguishing MP from natural debris and not detecting MP in the gut of ingested prey. Compared to the 3 % plastic occurrence rate found by Bråte et al. (2016), Lenz et al. (2016) analysed the stomach contents of plastic particles > 100 µm of 100 cods caught in coastal and offshore waters of the North Sea and the Baltic Sea. Of the 72 offshore North Sea cods analysed, 49 % were found to have MP in their stomachs. Whereas from the 28 coastal North Sea cods 14 % contained MP. The respective numbers for the Baltic cods were 26 % and 16 %. There was an overall tendency for higher likelihood of stomach plastic content for the offshore cod.

In the digestive tract and stomach of the fish, digestive fluids are in direct contact with the polymer. Such direct contact can enhance the mass transfer

of potential contaminants sorbed to the material. The gut retention time for North Sea cod have been reported to be 3.7 days (Daan, 1973), meaning that the plastic can possibly be retained in the intestinal tracts for around four days.

In the absence of plastic mass data in cod stomachs and guts the assessment is based on the following estimate: Body weight of a mature cod is 3000 g. An estimated maximum uptake is 10 MP particles with diameter 100 µm, which corresponds to 42 µgMP assuming spherical particles and a specific gravity of one. Steady state between ingestion and clearance rates is assumed, and a retention time of four days, leading to a plastic ingestion rate of 42 µg plastic/3000 gbw/4 days = 3.5 µgMP/kgbw/day.

Using an average stomach content in Atlantic cod of 2wt-% (Ursin et al., 1985) and a retention time of four days, the food ingestion rate is 0.02 gfood/gbw / 4 days = 5 gfood/kgbw/day. The plastic fraction in food is 3.5 µgMP/kgbw/day / 5 gfood/kgbw/day = 0.7 µgMP/gfood.

3.2.2 Predicted No Effect Concentration (PNEC)

For Predicted No-Effect Concentrations (PNEC), Danish *miljøkvalitetskrav* (MKK) for other surface waters, according to BEK no 1625 of 19/12/2017, are used. Furthermore, European Environmental Quality Standard (EQS) values for other surface waters, according to Directive 2013/39/EU and derived in accordance with Article 16 of the Water Framework Directive (2000/60/EC), for prioritized substances and certain other pollutants, are used. Additionally, EQS values for secondary poisoning from EQS 2005 and 2011 dossiers prepared Sub-Groups on Review of the Priority Substances List (under Working Group E of the Common Implementation Strategy for the Water Framework Directive), are used. These dossiers form the basis of EU EQS values for prioritized substances in the water framework directive. The information has been evaluated and peer-reviewed according to the procedure described in the documents.

In summary, MKK and EQS values for other surface waters are used as PNEC for the pelagic community in marine waters (copepod and cod), and EQS values for food intake (secondary poisoning) are used as PNEC for fulmar. When specific EQS values are available for food ingestion by fish these are used as PNEC, otherwise cod is assessed for the pelagic community.

The priority substances and certain other pollutants within the Water Framework Directive only comprise a limited number of the total amount of considered chemicals. It is not within the scope of this study to estimate PNEC or compile other toxicity values such as EC50 or NOEC and assign assessment factors. However, this would increase the number of toxicity data and included chemicals in the analysis and thus the completeness of the risk assessment.

3.2.3 Risk Quotient (RQ)

Finally, the risk quotients (RQ) are calculated as the ratio between the PEC and the PNEC:

$$RQ = \frac{PEC}{PNEC} \quad (\text{Eq. 1})$$

According to ECHA, if the RQ is below one (1), there is no risk as the PEC is below PNEC. On the other hand, $RQ \geq 1$ indicates there is a risk and the PEC exceeds the PNEC. A RQ is calculated for each chemical. If more than one chemical is comprised additivity of risk is assumed, and the RQs of the individual chemicals are summed.

3.3 Fate, exposure and uptake scenarios

3.3.1 Tiered approach

More or less realistic exposure scenarios can be defined to describe the risk of chemical additives associated with MP in the marine environment. Below are outlined two scenarios where the first is the most accurate and realistic representation of the real system. It is also stated which data and information are needed:

1. Most realistic: Identification of ingested types and amounts of plastic micro particles and macro fragments in the gut or stomach, or from exposure tests of marine organisms. Measurement of chemical constituents in plastic particles incl.; polymers, monomer residuals, additives, degradation products and sorbed environmental chemicals. Measurement/estimation of leachable amount of chemicals, which represents the bioavailable fractions.
2. Measurement of total amount of plastic micro particles and macro fragments in the gut or stomach of marine organisms. Theoretical identification of possible sources and assigning the total plastic amount to one source at a time. Estimation of types and amounts of chemical constituents (as above) representative of one source; either for i) chemical profile of original product, or ii) chemical profile of product particles after weathering and loss of solvents and volatile compounds. Theoretical quantification of bioavailable fractions; either a) total amount of chemicals are bioavailable, or b) an estimated leachable amount of chemicals represents the bioavailable fraction.

The choice of scenario depends on the available data. Scenario 2ia is the least data demanding. However, to increase realism as much as possible with the data at hand, scenario 2iib is used as the basis for the risk screening.

3.3.2 Plastic exposure scenario in this report

A worst-case scenario is a relevant and yet unlikely scenario that describes a situation primarily based on literature values, and where the occurrence, exposure and uptake are assigned high (critical) values. In the chosen scenario several assumptions can be considered worst-case, such as choice of one polymer at a time and use of maximum stomach content, where other assumptions have been adjusted to be more realistic, such as estimated leachable and bioavailable fractions.

The following assumptions are used:

- Maximum measured and estimated amounts of ingested macro and MP particles in the stomach/gut of fulmar and cod are used as exposure amounts.
- The ingested plastic amounts consist of only one polymer type, representing each of the described product group cases described below. In reality,

it is a mixture of different types of plastic containing a broader range of additives, however appearing at lower individual concentrations.

Before weathering:

- The plastic particles before weathering comprise residual monomers in amounts of: 0.1wt-% ethylene (case 1, LDPE); 0.1wt-% 1,3-butadiene and 0.1wt-% styrene (case 2, SBR tire); 0.01wt-% acrylic acid (case 3, acrylic paint); 0.000001wt-% vinyl chloride (case 4, PVC); no residual monomers (case 5, PUR); 0.5wt-% styrene (case 6, EPS); 0.1wt-% bisphenol A (case 7, PC).
- The plastic particles comprise chemical additives that are representative of the product group cases. Unless specific information is available, additives are estimated to be present in amounts of 0.1wt-%. Phthalate softener additives in PVC are assumed to be present in amounts of 50wt-%, and flame-retardants vary from 1-25wt-% in the various polymers (Babrauskas, 2012; Hahladakis, 2018; Hansen et al., 2013).

After weathering:

- The amount of remaining monomer, additives and degradation products after weathering, i.e. corresponding to the ingested particles, is assumed to be 10 %. Alternatively the remaining amounts could be 10 % in hard polymer materials (Case 1, 5, 6 and 7), and 1 % in soft polymer materials (Case 2, 3 and 4). Remaining amounts of phthalate softeners in PVC, and flame-retardants in all plastics are estimated to be 10 % of the amount in the plastic products. Remaining amounts of metal and silicate compounds in antifouling ship paint are estimated to be 10 %.
- For a plastic piece in the ocean, it is expected that the majority of solvents and volatile components have been leached and diluted in the surrounding saline water. Consequently, solvents and volatile additives are assumed no longer present.

Bioavailable fraction:

- A leachable fraction, estimated to 10 % of the remaining monomers and additives in the weathered plastic particles, is taken up in the bloodstream of the organisms following ingestion via water or secondary poisoning.

If these conservative and precautionary risk scenarios conclude positive, i.e. $RQ > 1$, then more realistic scenarios, with more detailed process descriptions and data, need to be considered.

3.4 Cases relevant for the marine environment

All raw materials for Danish plastics converters are imported, and no manufacture takes place in Denmark. The distribution of plastics raw materials in Denmark by plastics type is similar to the total European plastics production. The total amount of plastic raw material in Denmark was approximately 583,000 tonnes in 2014. Some of the raw materials are not traded in pellet or dust form, but rather as liquid resins (e.g. the epoxy resins and some of the polyesters) and the total use of solid plastics raw materials is likely in the range of 500,000-550,000 t/y (MST, 2015).

Several thousand different additives are used in the polymer industry. Polymerization additives become part of the polymer (e.g. cross linking agents, curing agents, inhibitors, initiators), or are necessary to preserve the stability of the polymer. Other additives are combined with a polymer substance to form a mixture with the particular mechanical and other properties needed for the formation of articles. These latter “inherent” additives, e.g. flame-retardants and softeners, are incorporated into the final polymer matrix (EC, 2012).

In collaboration with the industry for PUR and PC, seven cases with different polymers that represent the most significant exposures of MPs and inherent chemicals have been defined. These represent high-risk cases for marine organisms or ecosystems. For each of these cases product groups with significant use and release to the marine environment have been identified.

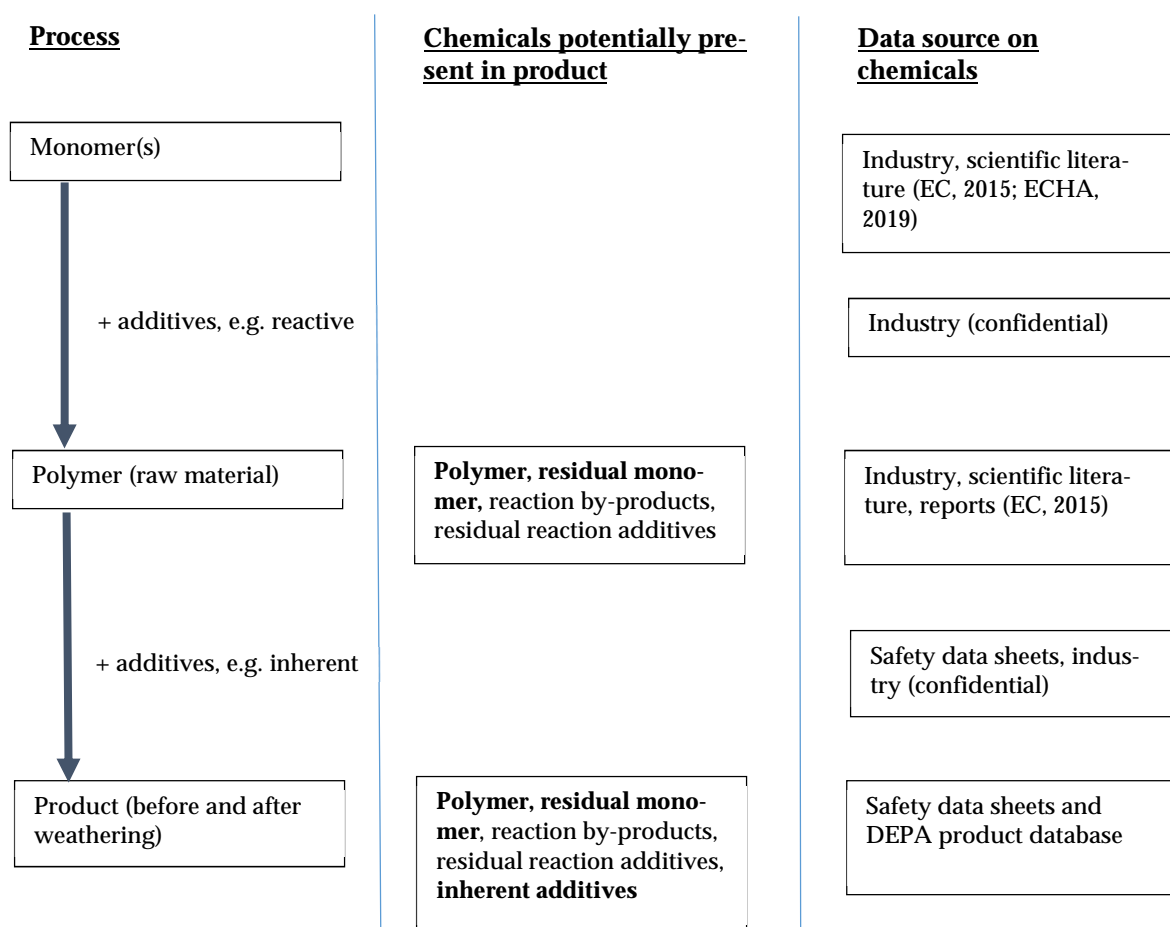


Figure 4 Simplified scheme for processes, included chemicals and possible data sources.

Information on types and amounts of used additives is typically confidential. The Danish downstream distributors and manufacturers do not have access to this information.

Identifying data sources is also a challenge as bottom up or top down approaches have been employed, and there are often missing links between connecting data information from different data sources. For example, it is most often not possible to identify used amounts of specific additives, due to confidentiality.

General information on available additives from databases, reports and web-sites may not be appropriate to use, unless it reflects Danish conditions with respect to bans and substitutions. One approach is to use safety data sheets for Danish manufacturers, when available, for the polymers themselves and for the relevant products. According to the Danish Working Environment Authority (Arbejdstilsynet) safety data sheets must be prepared for mixtures that do not meet the criteria for classification as hazardous in accordance with Titles I and II of the CLP Regulation no. 1272/2008, but contain in an individual concentration of $\geq 1\%$ by weight for non-gaseous preparations and $\geq 0.2\%$ by volume for gaseous preparations, at least one substance posing human health or environmental hazards. This implies that additive residuals and reaction by-products that typically are present in the ppm range will not be included in safety data sheets.

Data and information from web sites such as ECHA (2019) have been used. These maps plastic additives including a method for comparing the release potential of plastic additives.

The chemical finger print of the plastic polymers (residual monomers, reaction by-products, chemical additives from the polymerisation process and chemical additives from the product manufacturing process) is thus based on an identification of typical used additives and a quantification as described below. Additional data and information are compiled from communication with the plastic industry, the scientific literature, manufacturers, reports and web sites. The additives that are listed below are thus assessed to be present in plastic on the Danish market. Many more have been used historically but have been banned, although they may still be found in older products and in imported products.

The chemicals in the products in the seven cases are described in the following and summarized in Table 4. The results of the risk assessments (RQs) are listed in Table 5.

3.4.1 Case 1: Low-density polyethylene (LDPE) in various products

Net import of raw material for PE and LDPE was 120,129 t/y in 2014, corresponding to 21 % of the annual total for all polymer types (MST, 2015, statistics Denmark: external trade statistics).

LDPE is widely used in plastic bags, containers, bottles, tubing and personal care products. Use of MP in personal care products has received considerable attention during the latest years, and the members of the Danish plastics trade organisation have either phased out, or never used MP in their personal care products (Kosmetik- og hygiejne trade organisation, personal communication, 2018).

For secondary MP in the Baltic Sea Region, the dominant fraction, based on numbers, are plastic pieces with sizes between 2.5 and 50 cm (24 %) having an average frequency of 34 items per 100 m of coast line, followed by cigarette butts (10 %) and other items such as plastic bottle caps/lids (5 %), foam sponges (5 %), ceramic/pottery items (5 %) and plastic (shopping) bags (4 %) (Arcadis, 2014). The use of LDPE in bud sticks has decreased by replacement with e.g. cardboard (Kosmetik- og hygiejne trade organisation, personal communication, 2018).

Ethylene (CAS no 9002-88-4) is used as monomer in amounts of 98-99wt-% in the production of the plastic resin. There are different processes to separate and remove unreacted ethylene, which typically is below 0.1wt-%. This amount is considered in the scenario for LDPE.

According to the scientific literature and from reports several additives may be added to preproduction pellets or powders, and others may be added in conversion steps (e.g. Charrier, 1991: Polymer materials and processing – Plastics, Elastomers and Composites; Jean-Michel Charrier; Hanser publishers, 1991).

Zhou (1998) found the following concentrations of residual additives in LDPE samples: Antioxidant: 2,6-Di-tert-butyl-4-methylphenol (BHT) (CAS no 128-37-0) (approx. 0.1wt-%); Antioxidant: 2,6-Di-tert-butyl-4-ethylphenol (BHEB) (CAS no 4130-42-1) (approx. 0.1wt-%); Antioxidant: 2,2'-ethylidenebis(4,6-di-tert-butylphenol) (Isonox 129) (CAS no 35958-30-6) (approx. 0.1wt-%); Antioxidant: Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) (CAS no 2082-79-3) (approx. 0.1wt-%); Antioxidant: Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (Irganox 1010) (CAS no 6683-19-8) (approx. 0.1wt-%).

Lead and lead compounds (CAS no 75-74-1 and several others) are used in pigments in all types of plastics being coloured. Lead chromate molybdate sulfate can be used in polyethylene, and lead sulfochromate yellow (CAS no 1344-37-2) in LDPE in estimated amounts of 0-5 wt-%. Plastic coloured with lead pigments will typically contain 1-3 wt-% lead. The lead is bound in the plastic matrix and the amount released by wear and tear can be assessed as small compared to the total amount in the product (Hansen et al., 2013).

3.4.2 Case 2: Styrene butadiene rubber (SBR) in car tires

Safety data sheets from non-Danish manufacturers have the following tire composition: Styrene butadiene (SBR) polymer (1,3-butadiene (75 %), Styrene (25 %) (9003-55-8) (60-80wt-%). Distillates (petroleum), solvent-refined heavy paraffinic (oil filler) (64741-88-4) (14-17wt-%) or Petroleum distillates, hydrotreated heavy naphthenic (64742-52-5) (20-40wt-%).

According to Carraher (2018) the typical composition of a modern tire tread is elastomer: natural rubber (30wt-%), elastomer: styrene-butadiene rubber (30wt-%), reinforcing filler: carbon black (27wt-%), extender: aromatic oil (5wt-%), accelerator: stearic acid (2wt-%), antioxidant: aryl diamine (2wt-%), accelerator: zinc oxide (2wt-%), vulcanizing agent: sulfur (1wt-%), antioxidant: antiozonante (0.5wt-%), processing aid: paraffin wax (0.5wt-%), delayed accelerator: N,N-diphenyl guanidine (0.1wt-%).

Jusli et al. (2014) states the following composition of waste tire rubber granules: SBR (48wt-%), carbon black (47wt-%), extender oil (1.9wt-%), zinc oxide (1.1wt-%), stearic acid (0.5wt-%), sulfur (0.8wt-%), accelerator (0.7wt-%).

US tire manufacturers association has a composition of passenger/light truck tires: natural rubber (19wt-%), synthetic polymers (24wt-%): mainly butadiene rubber and styrene butadiene rubber, steel (12wt-%), textile (4wt-%): polyester cord fabrics, rayon cord fabric, nylon cord fabric and aramid cord fab-

ric, fillers (26wt-%): carbon black, amorphous precipitated silica. Furthermore, antioxidants, antiozonants, curing systems (sulphur, zinc oxide) (14wt-%).

Kreider et al. (2010) states a physical and chemical characterization of tire-related particles: plasticizers and oils (10-19wt-%), polymers (16-46wt-%), carbon black (11-19wt-%), minerals (16-61wt-%). Furthermore Kreider et al. (2010) analysed the content in tire particles of metals generally not associated with tires. Amounts of metals are: lead (0.005wt-%) and nickel (0.004-0.005wt-%), which are among the Water Framework Directive priority substances.

Highly aromatic oils used as extender oils or softeners in the tire-manufacturing process are rich in PAHs, many of which are classified as carcinogenic/mutagenic toxins both to humans and the aquatic environment. The PAH concentration in these oils ranges between 10 to 30 %. As a measure to phase out these PAH-rich oils and replace them with low-PAH alternatives such as mild extracted solvates and treated distillate aromatic extracts, their use has been regulated by EU Directive 2005/69/EC, which forbids the oils in rubber manufacturing. Any new tire or tire tread used for re-treading manufactured after first January 2010 may not contain any extender oil with more than 1 mg/kg benzo(a)pyrene (BaP) or more than 10 mg/kg of the sum of the eight PAHs: BaP, benzo(e)pyrene (BeP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), benzo(k)fluoranthene (BkF), and dibenz(a,h)anthracene (DBa,h-A). Tires that were manufactured prior to this date are not covered by these threshold values. The replacement of oils is estimated to reduce the PAH emission originating from tire-tread-wear by 98 %. Another material known to contain PAHs used in tire manufacturing is carbon black. Carbon black is a form of elemental carbon used as reinforcement material in the tire rubber to give the tire its desired properties in abrasion resistance and tensile strength (Sadiktsis et al., 2012).

Sadiktsis et al. (2012) analyzed three summer tires, two non-studded winter tires and three studded winter tires. The tire samples had previously been used in road simulation studies. All of the analyzed tires were manufactured before January 2010. They found average contents of PAHs (only PAHs with EU-EQS values are stated here): BaP (0.0005wt-%), BbF (0.0002wt-%), BkF (0.00004wt-%), benzo(g,h,i)perylene (B(g,h,i)P) (0.0018wt-%), indeno(1,2,3-cd)pyrene (I(1,2,3-cd)P) (0.0007wt-%).

Kreider et al. (2010) also analyzed the content in tire particles of PAHs that are most common in the environment and that IARC considers to be carcinogenic. Content of PAHs that are on the list of priority substances are: BaP (0.00003-0.0013wt-%), anthracene (0.00001-0.0007wt-%), fluoranthene (0.0001-0.0082wt-%), naphthalene (0.00002-0.0006wt-%), BbF (0.00004-0.0007wt-%), BkF (0.000002-0.0007wt-%), B(g,h,i)P (0.0002-0.0004wt-%), I(1,2,3-cd)P (0.00002-0.0005wt-%). The analysis was performed for on-road and road simulator laboratory tests, the latter using actual road pavement.

Both PAH studies used abraded tire particles that may contain metal and PAH contributions from other sources such as bitumen and diesel and gasoline exhaust. However, as recycled rubber is broadly used in tires the external content may be considered as part of the tire material.

3.4.3 Case 3: Acrylic paints for ships and leisure boats

Acrylics are used in window framings, corrugated plates, lighting sockets, road signs, building facades, advertising signs, bathtubs, sinks, spectacle frames, contact lenses, big-screens, protection screens, watch glasses and windscreens for busses among other things. Acrylics are also used as binders in colorants, lacquers and glue. In this case, focus is on ship paints.

Releases of secondary MP to the aquatic environment from ship paints are estimated to contribute approximately 3 % of the total MP releases in Denmark (MST, 2015). Paint releases to the aquatic environment are assessed to contribute with 40-480 t/y corresponding to 21-240 t/y to the aquatic environment after wastewater treatment plant (MST, 2015).

MPs are formed from abrasion and maintenance of marine paints. A significant proportion of the releases occur directly to aquatic environments. In addition, MPs may be formed by the releases of self-polishing antifouling paints when the ships are in the water.

As representative manufacturer of ship paints used in Denmark Hempel is used; "Hempel is a world-leading coatings supplier for the decorative, protective, marine, container and yacht markets." The products Hempel Globic 6000 and Hempel Dynamic 8000 are used as examples of antifouling ship paints:

http://www.hempel.com/sitecore/content/Global/Products/product-directory/group-assortment/75000-79999/globic-6000-75950?sc_lang=en
- an example of nano acrylate technology

<http://www.hempel.com/en/products/dynamic%208000%2079450>

In Hempel's antifouling Dynamic 8000, and Hempel's antifouling Globic 6000* the following ingredients are used:

Copper (I) oxide (1317-39-1) (25-50wt-%)¹

Xylene (1330-20-7) (10-25wt-%)

Zinc ethylene-1,2-bis-dithiocarbamate (zineb) (12122-67-7) (3-5wt-%)¹

Ethylbenzene (100-41-4) (3-5wt-%)

Tetraethyl silicate (78-10-4) (1-3wt-%)¹

C10 aromatic hydrocarbons, <1wt-% naphthalene (64742-94-5) (1-3wt-%)

Copper pyrithione (14915-37-8) (1-3wt-%)¹

Zinc oxide (1314-13-2) (1-3wt-%) (10-25wt-%)*¹

n-butanol (71-36-3) (1-3wt-%)

Cupric oxide (1317-38-0) (1-3wt-%)¹

Copper (metallic) (7440-50-8) (<1wt-%)¹

4-methylpentan-2-one (108-10-1) (1-2.6wt-%)*

The metal and silicate compounds¹ in antifouling ship paint are expected to remain in the product after hardening. Ten percent of the original amount in the finished product is estimated to be present after weathering.

Other chemicals in the formulation are considered VOCs (vapour pressure > 0.01 kPa), but they are estimated not to be present after weathering.

The binder, a polymer, often referred to as resin constitutes acrylic polymers, which include the polyacrylates. The acrylate monomers that are used to produce polyacrylates, are completely consumed in the polymerisation process and only contain trace levels of the polymerisation by-products acrylic acid and esters (OECD, 2005). It is assumed that 0.01wt-% of acrylic acid (CAS no 79-10-7) remains in the plastic particles before weathering.

3.4.4 Case 4: Polyvinyl Chloride (PVC) in cables, cords, linoleum flooring also on ships

PVC is not one single material but constitutes a material group where the content of softener can be up to 50wt-%. Non-softened and lightly softened PVC is termed hard PVC or PVC-U, and is relatively strong with good structural stability. The more rubbery types, constituting 20-50wt-% softener are termed soft PVC.

The percentage of PVC on the Norwegian market is estimated to be 10.7 %, and the specific gravity is 1.16 – 1.30 (Sundt et al., 2014).

Vinyl chloride (CAS no 75-01-4) is the monomer in PVC and is used in amounts of approx. 50wt-% (Lithner et al., 2011). Residual vinyl chloride in PVC resins and products are on the ppb level, e.g. 10 ppb (Borrelli et al., 2005).

Arsenic and arsenic compounds (CAS no 7440-38-2; and others), are used to produce 10,10'-oxybisphenoxarsine (OBPA, CAS no 58-36-6) which is a antimicrobial (accounting for 70 % of the demand for antimicrobials in plastics). Plasticised PVC have a particular susceptibility to microbial attack and is the main plastic in which biostabilizers are incorporated. In most cases, biostabilizers are formulated with a carrier, usually a plasticiser, at a concentration of 2 to 20wt-% active ingredient. For OBPA is recommended a concentration of 0.03-0.05wt-% for plastics. OBPA will likely remain bound without significant migration in the plastics, and will potentially be released mainly by wear and tear (COWI 2013).

Bis-(2-ethylhexyl)phthalate (DEHP) (CAS no 117-81-7) is a plasticiser used in amounts of 30-60wt-%, and is typically used together with other phthalates. Not chemically bound, and will potentially migrate in the range of 0.1-1wt-% per year or less. Wear and tear is of minor importance (COWI 2013).

Benzyl butyl phthalate (BBP) (CAS no 85-68-7) is used as plasticiser typically in flooring in amounts of 10-30wt-%, and often together with other phthalates. Not chemically bound, and migration and release is analogous to DEHP (COWI 2013).

For many years, Dibutyl phthalate (DBP) (CAS no 84-74-2) has been one of the dominant plasticisers for flexible PVC. DBP is always used in combination with other phthalates, in amounts typically be below 10wt-%. Not chemically bound, and migration and release is analogous to DEHP (COWI 2013).

Diisobutyl phthalate (DiBP) (CAS no 84-69-5) is a plasticizer and always used in combination with other phthalates. Not chemically bound, and migration and release is analogous to DEHP. DiBP is registered in concentrations up to 0.2wt-%. DiBP is in several products registered in concentrations down to below 0.001wt-% (Hansen et al., 2013).

PAHs are usually present as a complex mixture of several hundred congeners. PAHs are present as impurities in plasticisers (e.g. mineral oil and coal based extender oils) and carbon black. PAHs may be present in materials used for construction work, e.g. flooring material, and generally in plastic products coloured black. In Germany a survey of various products (about 5000 samples) registered up to 530 mg/kg (0.053wt-%) for BaP, up to 9300 mg/kg for sum of 16 PAHs (USEPAs PAH list), and up to 2483 mg/kg for the sum of BaP, BaA, CHR, BbF, BkF, DBah-A. In most of these products, however, PAHs were non-detectable or present only to a very low degree. For some products, significant release can be expected (Hansen et al., 2013).

Chromium and chromium compounds (CAS no 1333-82-0, and several others) are components in pigments (yellow, red and green colours). For pigments, concentrations in the range of 0.01 - 0.29wt-% have been registered. It is solid bound in the plastic and release is by wear and tear of product (COWI 2013).

Cadmium and cadmium compounds (CAS no 7440-43-9, and others), is used in heat and UV stabilizer in PVC, and in pigments in all coloured plastics. Concentration in PVC is approx. 0.01-1wt-% as pigment, and approx. 0.1wt-% as stabilizer. Cadmium is bound in the plastic matrix and release potentially occurs by wear and tear of product.

Lead and lead compounds (CAS no 75-74-1 and several others) is used as heat and UV stabilizer for PVC (50 % of all stabilisers used for PVC). Furthermore, lead is used in pigments in all types of plastics being coloured. Lead chromate molybdate sulfate can be used in both rigid and plasticised PVC in rough estimates of 0-5wt-%. Plastic coloured with lead pigments will typically contain 1-3wt-% lead, while stabilized PVC will contain about 2wt-% lead. The lead is bound in the plastic and the amount released by wear and tear can be assessed as small compared to the total amount in the product (Hansen et al., 2013).

Medium-chain chlorinated paraffins (MCCP) (CAS no 85535-85-9) is a plasticizer and flame-retardant, and is used in amounts of 9-13 wt-%. MCCP is not chemically bound, and it is estimated that significant release through migration will take place during lifetime of plastic product.

Nonylphenol and its ethoxylates (CAS no 25154-52-3 general group). The amounts in the plastic are not known, but any residuals are not chemically bound and may migrate in the product (Hansen et al., 2013). Nonylphenol compounds are used as antioxidant and UV stabilizer in amounts of 0.05-3wt-%, and furthermore nonylphenol (barium and calcium salts) are used as heat stabilizers in amounts of 0.5-3wt-% (Hahladakis et al. (2018).

Octylphenol and its ethoxylates (CAS no 140-66-9, 1806-26-4, 9004-87-9, 9036-19-5, 9063-89-2, 11081-15-5, 68987-90-6, 69011-84-3). Most of the 4-tert-octylphenol in the resins is chemically bound and cannot be released even on subsequent chemical or biological degradation. The resins may contain a small proportion, approx. 3-4wt-%, of unreacted 4-tert-octylphenol, which may be released from the plastic (Hansen et al., 2013). Octylphenol is used as

antioxidant and UV stabilizer in amounts of 0.05-3wt-% (Hahladakis et al., 2018).

Organic tin compounds (tributyltin, trifenyln, dibutyltin) (CAS no 76-63-1, and others) is used as biocide, as trisubstituted tin compounds: tributyltin, trifenyln. Dibutyltin compounds were used as stabilizers in colourless and/or transparent PVC plastic articles, such as roof panels/windows, transparent partitions for clean rooms, packaging (blisters), containers, bottles, films (wrapping). Dibutyltin used as stabiliser is normally added in amounts of 0.001-1wt-%. Antimicrobial products based on tributyltin oxide and tributyltin maleate are formulated at concentrations around 1wt-% and 25wt-% respectively and generally further diluted by mixing with other ingredients. Tributyltins can be present as impurities in mono- and dibutyltin stabilisers for plastics (up to 1wt-%), but their content is voluntarily controlled by industry to $\leq 0.67\text{wt-\%}$ (as tin). Dibutyltin compounds have been in use for many years, but are now being restricted. Some uses (e.g. roof panels/windows etc.) will remain in use for many years. From 1 July 2010 new products with $>0.1\text{wt-\%}$ tributyltin (as tin) were banned. Not solid bound and will migrate, and will also be released by wear and tear (Hansen et al., 2013).

Trichloroethylene (CAS no 79-01-6). Intermediate or chain transfer agent for controlling molecular weight in the manufacture of PVC. No data on amounts in PVC products, but insignificant concentrations could be expected. Directive 2003/36/EC restricts the concentration to $<0.1\text{wt-\%}$. Trichloroethylene is very volatile, and will readily migrate and evaporate from the products while new (Hansen et al., 2013).

3.4.5 Case 5: Polyurethane (PUR) rigid foam in building insulation

The PUR case will be used to highlight the problem regarding occurrence of residual monomers and the formation of degradation products that may be hazardous to the marine environment. The Percentage of PUR on the Norwegian market is estimated to be 7.3 %, and the specific gravity is 1.2 (Sundt et al., 2014).

Flexible PUR (e.g. for furniture upholstery and mattresses) is largely TDI¹-based, with about 10 % MDI², and Rigid PUR (e.g. for insulation, district heating tubes, refrigeration, construction) is purely polymeric MDI-based (MST, 2014). In the marine case , rigid PUR and thus MDI is considered.

Safety Data Sheets from Danish manufacturers of building construction PUR foam, e.g. Dana Lim, state the following reagents and ingredients with CAS no and wt-% (minimum - maximum intervals) in the products:

Reagents

- 4,4'- methylenediphenyl diisocyanate (MDI) (CAS no 101-68-8), isomers and homologues (5-60wt-%)

¹ Toluene diisocyanate (TDI) is an aromatic diisocyanate with the formula $\text{CH}_3\text{C}_6\text{H}_3(\text{NCO})_2$. Six isomers are possible, of which 2,4-TDI (CAS no: 584-84-9) and 2,6-TDI are commercially the most important.

² Methylene diphenyl diisocyanate (MDI) is an aromatic diisocyanate with the chemical formula $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2$ where the two aromatic rings are connected by a methylene group. Three isomers - 2,2'-MDI, 2,4'-MDI, and 4,4'-MDI (CAS no: 101-68-8;) - exist.

- Oligomer MDI: oligomeric reaction product (CAS no 32055-14-4) (10-15wt-%) of formaldehyde with aniline and phosgene. Formaldehyde (CAS no 25214-70-4) is an intermediate and no data on residue amounts are available.
- Propane-1,2-diol, propoxylated (CAS no 25322-69-4) (5-10wt-%)

The reagents harden to the final PUR. The total extractable amount from a thermoset plastic is estimated to be less than 5 % of the total amount of reagents, as is common for most thermosets. These residuals are oligomers of the isocyanates (Marand et al., 2004). An amount of 0.1wt-% oligomer MDI remaining in the plastic is assumed prior to environmental weathering.

Other ingredients

- C14-17 chloroalkanes (CAS no 85535-85-9) (5-60wt-%). The chloroalkanes evaporate during foaming and a residual amount of 1wt-% is assumed prior to weathering
- Tris(2-chlorisopropyl)-phosphate (CAS no 13674-84-5) (2.5-20wt-%). A similar chemical tris(2-chloroethyl)phosphate (TCEP) (115-96-8) (0-6 wt-%), is used as plasticiser and viscosity regulator with flame-retardant properties in e.g. the building industry in roof insulation. TCEP is not chemically bound and may be regarded as semi-volatile, and the major part of the substance will probably leach to the surface. Wear and tear will also take place but is of minor importance (Hansen et al., 2013). A residual amount of 0.5wt-% is assumed prior to weathering
- Isobutane (CAS no 75-28-5) (1-25wt-%). Will evaporate
- Propane (CAS no 74-98-6) (1-25wt-%). Will evaporate
- Dimethylether (CAS no 115-10-6) (2-25wt-%). Used as solvent, and will evaporate.

Brominated flame-retardants (CAS no 32534-81-9 (PeBDE), 32536-52-0 (OBDE), 1163-19-5 (DBDE), 25637-99-4 (HBCD); 79-94-7 (TBBPA), 3194-55-6, 134-51-7, 134237-52-8, etc.) can be either reactive (chemically bound in the material) or additive (not chemically bound in the material). While TBBPA generally is used as a reactive flame-retardant, the other mentioned brominated flame-retardants are additives. For thermoplastics, non-reactive flame-retardants (additive) are usually used, while reactive flame-retardants are normally used for thermosetting plastics (epoxy, unsaturated polyester and polyurethane). Additive flame-retardants can be released from the plastic material since they are not chemically bound. For the reactive flame-retardant release is limited since they are chemically bound within the polymer (Hansen et al., 2013).

Production of PeBDE in the EU ceased in 1997. Usage in EU has been declining during the second half of the 1990's and was estimated to be 300 metric tonnes in year 2000, used solely for PUR production. The use of PentaBDE was banned in the EU in 2004 through the Council directive 2003/11/EC relating to restrictions on the marketing and use of certain dangerous substances (SFT, 2009). While the production, placing on the market and use of TeBDE and PeBDE are prohibited, some recycling of articles containing these substances and produced before introduction of the ban cannot be excluded (Stockholm Convention, 2019b). Hahladakis et al. (2018) states a brominated flame-retardant content of 3-25wt-%. The most common use, accounting for 95-98 % of PeBDE since 1999, has been in PUR, which may contain between 10 and 18wt-% of the PeBDE formulation (UNEP, 2006). A PeBDE amount of 15wt-% prior to weathering is used.

Mercury and mercury compounds (CAS no 55-68-5, and others) is used as catalyst in manufacturing of PUR-polymers may be present as contaminant in products such as gaskets and seals, as encapsulant for electronic assemblies, in vibration dampers, water resistant coatings and concrete sealants, for boat repair and repair on conveyor belts, and in flooring. New products will typically contain 0.1-0.3wt-% mercury. An example is an amount of 0.1-0.2 wt-% mercury in polyurethane floor installed in the US between 1960s-1980s (Hansen et al., 2013). The mercury is not bound and will migrate, and elemental mercury will vaporise from the plastic material, e.g. flooring. The presence of mercury has not been confirmed by Danish data and is omitted in this study.

Bis(tributyltin)oxide (TBTO) (CAS no 56-35-9) is used in products such as flooring and tiles. Today TBTO is only used as intermediate, but previously as an antimicrobial agent. Tributyltins can be present as impurities in mono- and dibutyltin stabilisers up to 1wt-%, but their content is voluntarily controlled by industry to ≤ 0.67 wt-% (as tin). From July 2010 new products with >0.1 wt-% (as tin) were banned. A volatile compound that is not bound in the plastic matrix, and can thus migrate and also be released by wear and tear (Hansen et al., 2013).

2,2'-dichloro-4,4'-methylenedianiline (MOCA) (CAS no 101-14-4) is used as curing agent, cross-linker and chain extender and the amount of un-reacted MOCA is estimated to be in the range of 0.01 wt-% and 4 wt-%. Solid bound from reaction, but unreacted MOCA can migrate (Hansen et al., 2013).

Hydrazine (CAS no 302-01-2; 7803-57-8) is used as a crosslinker and chain extender in PUR. Hydrazine is solid bound, and due to its high reactivity, no intermediate residues are expected in the end products. Release is probably only by wear and tear (Hansen et al., 2013).

Nonylphenol and its ethoxylates (several CAS no's) is used as emulsifier in PUR foam. The amounts in the plastic are not known, but any residuals are not chemically bound and may migrate in the product (Hansen et al., 2013).

Another formulation in Lithner (2011) for rigid PUR foam for isolation was obtained from the Chemicals industry listing approximate content of monomers and blowing agents of 31 wt-% propylene oxide, 13 wt-% sorbitol, 52 wt-% crude MDI, and 4 wt-% cyclo-pentane. In this study the formulation by the Danish manufacturer is chosen.

PUR has relatively low resistance to biodegradation and can furthermore be degraded by heat, oxidation, light, hydrolysis, mechanical shear and various pollutants. Furthermore, degradation is relatively slow in the marine environment, where degradation mainly is likely to occur by solar radiation and slow thermal oxidation. In some situations, the time for complete degradation could be several hundred years (Lithner et al, 2011).

Chemicals of concern that are or could be formed or left in MDI- and TDI-based products during handling, production and end-of-life are assessed to be: i) Residual monomers of MDI and TDI, ii) Depolymerisation of PUR at elevated temperatures resulting in liberation of isocyanate monomers (e.g. TDI and MDI), and iii) Aromatic diamines (methylenedianiline MDA, CAS no 101-77-9, and toluene diamine TDA, CAS no 95-80-7) derived from MDI and TDI by degradation either by photo-oxidation or hydrolysis (MST, 2014).

MDI and TDI monomers have been identified in a number of Danish EPA projects. However, ISOPA and EuroPUR (European Association of Flexible Polyurethane Foam Blocks Manufacturers) state that any findings of MDI and TDI in PUR products can be created by the analytical method and, therefore, constitute artefacts rather than actual presence of MDI and TDI in such products. MST (2014) argues that data are too scarce for making general conclusions regarding presence of residual TDI and MDI (or MDI and TDI as a result of degradation) in products where MDI and TDI has been used during manufacturing.

Lewandowski et al. (2005) conclude that small amounts of reaction products MDA and TDA are released during MDI and TDI polymerization and may be present in newly finished PUR foam parts. Analytical results for sampling of freshly produced foam parts gave 2.3-15.4 mg/kg at demold, and 0.5-4.6 mg/kg after 8 hours of the most abundant MDA isomer, namely 2,4'-MDA. For the most abundant TDA isomer, 2,6'-TDA, the concentrations were 65.6-109.5 mg/kg at demold, and 8.6-21.3 after 8 hours. In this study, it is concluded that MDI residuals (MDA) in the weathered plastic fragments found in the marine environment will be approx. 0.01 mg/kg (0.000001wt-%).

According to Lithner (2011) there are several toxic monomers in these types of PUR foams used in building materials, but the amounts are probably negligible.

Babrauskas (2012): TCPP: Most polyurethane insulations including flexible-faced laminate, panels, block and injected foams contain TCPP, an additive chlorinated flame-retardant. In addition, TCPP is often used in polyisocyanurate (isocyanurate-modified polyurethane) board. TCPP is used at 2-25wt-% in boards and 5wt-% levels in foam (EC, 2008b). TCPP is also used in flexible foam for furniture and bedding (EC, 2008b; Van der Veen & de Boer, 2012).

3.4.6 Case 6: Expanded polystyrene (EPS) foam in Building insulation and packaging

The specific gravity of expanded polystyrene (EPS) ranges from 0.01 to 1.05 (Sundt et al., 2014). Danish companies do not use chemical additives in their handling of the PS raw material. It can however not be ruled out that additives are used in the production of the raw material. The specific additives, their used amounts and the possible residual amount in the raw material is not known according to the Danish Plastics Federation (personal communication, 2018).

The main component of polystyrene is styrene and as result of incomplete polymerisation during production, monomers and also other short chain styrene oligomers have been shown to leach out of EPS (Ahmad and Bajahlan 2007; Farrelly and Shaw 2017). Styrene oligomers as impurities is expected to be found primarily in lower grade EPS products, e.g. in building materials, and to a lesser extent in EPS produced for food packaging. The leaching of styrene is increased by the crack formations as results of thermal- and photo-oxidation induced aging processes.

Garrigos (2004) evaluated several extraction methods for the determination of residual styrene monomer in polystyrene granules used in toys. Mean styrene concentrations in two investigated polystyrene resins were from 0.003 wt-% and up to 0.6 wt-%, depending on the extraction method.

Flame-retardants are added around the world in EPS, e.g. in construction materials and electronic products (Zhao et al., 2010). The two major flame-retardants currently used in building insulation are hexabromocyclododecane (HBCD or HBCDD) and tris (1-chloro-2-propyl) phosphate (TCPP) (Babrauskas, 2012). HBCD is/was typically used in polystyrenes at levels of up to 1wt-% in expanded polystyrene (EPS) and up to 5wt-% in extruded polystyrene (XPS). While the use of HBCDs in EPS and XPS materials for other purposes than construction material and electronical housings is considered to be small (UNEP, 2011), they have been detected in packaging materials and EPS buoys (Rani et al. 2014; 2017). In the formulation of flame-retarded EPS beads the HBCD concentration is 0.7wt-% according to COWI (2013). HBCD is not bound in the plastic and a significant fraction of the chemical will probably leach to the surface and the environment. Wear and tear will also take place (Hansen et al., 2013). In a European Union study, uses for building insulation were estimated to account for 87wt-% of all HBCD releases to the outdoor environment (ECHA, 2009).

HBCD is listed in Annex A to the Stockholm Convention (2019a) with specific exemption for production and use as flame-retardant in EPS and XPS in buildings until August 2017. After this, data EPS and XPS may occur in the environment and furthermore significant amounts of HBCD is present in recycled PS packaging (Abdallah et al., 2018). In this scenario, a HBCD amount of 1wt-% in EPS prior to weathering is used.

Smith (2002) found the following extractable amounts of additive residues in polystyrene: UV stabilizer: Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl (Tinuvin P) (CAS no 2440-22-4) 0.008-0.01 wt-%; UV stabilizer: Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (Tinuvin 770) (CAS no 52829-07-9) 0.001-0.006 wt-%; Antioxidant: Tris(Nonyl-Phenyl-Phosphite (wytox) (CAS no 26523-78-4) 0.001 wt-%; Antioxidant: Irganox 1076) (CAS no 2082-79-3) 0.005-0.01 wt-%.

Boric acid (CAS no 10043-35-3, 11113-50-1) can be used as flame-retardant for polystyrene beads expanded to polystyrene foam. Boric acid may migrate but the concentration is not known (COWI 2013), and therefore not included in this analysis.

3.4.7 Case 7: Polycarbonate (PC) in construction materials

Polycarbonate is among other applications used for bottles, cabinets, safety helmets, toys, lighting glass, bulletproof screens, protection screens, medical equipment and for other technical purposes. Furthermore, PC is used in household equipment for coffee machines, shavers, hair dryers and for CDs and DVDs. PC is a thermoplastic with particularly good impact strength. PC can be produced glass clear.

Bisphenol A (BPA) (CAS no 80-05-7) is a monomer used in processing. The residual content in baby bottles purchased in Singapore has been reported to range from 0.0003 to 0.0141 wt-%. Bottles purchased in Washington ranged from 0.0007 to 0.0058 wt-%. Based on the chemical properties of bisphenol A, it should be regarded as a semi-volatile compound able to migrate out of plastics. The major part of the substance will probably be released by leaching to the surface and wear and tear will be of minor importance COWI (2013).

Bisphenol A is used in amounts of approx. 50wt-% when used with diphenyl carbonate (CAS no 102-09-0) (approx. 50wt-%). When used with phosgene (CAS no 75-44-5) (approx. 30wt-%), bisphenol A is used in amounts of approx. 70wt-% (Lithner et al., 2011). The reagents are volatile and 0.1wt-% are assumed remaining in the plastic before environmental weathering.

Lead and lead compounds (CAS no 75-74-1 and several others) are used in pigments in all types of plastics being coloured. Plastic coloured with lead pigments will typically contain 1-3 wt-% lead. The lead is bound in the plastic matrix and the amount released by wear and tear can be assessed as small compared to the total amount in the product (Hansen et al., 2013).

3.5 Risk evaluation

In Table 4 the amounts of bioavailable residual monomers and additives and reaction products in weathered MP in the marine environment are compiled for the seven cases with different polymer types and associated product groups. The amounts are estimated from the outlined scenario for exposure.

In Table 5 the Predicted Environmental Concentrations (PECs), Danish *Miljøkvalitetskrav* (MKK), European Environmental Quality Standards (EQS) and Risk Quotients (RQs) are compiled for the seven plastic cases. Estimated PEC for chemicals are based on the derived exposures of MP in marine water, i.e. 42 mgMP/m³, and ingested micro- and macro plastic particles in food/prey for cod: 3.5 µgMP/kgbw/day and 700 µgMP/kgfood, and for fulmar: 1 gplastic/kgbw/day and 3430 µgplastic/kgprey.

As an example, the PECs for lead in LDPE particles, in the uppermost rows in Table 5, are calculated as:

$$\text{PEC(copepod)} = 0.0001 \text{ µglead/µgMP} * 42 \text{ µgMP/L} = 0.0042 \text{ µglead/L}$$

$$\text{PEC(cod)} = 0.0001 \text{ µglead/µgMP} * 42 \text{ µgMP/L} = 0.0042 \text{ µglead/L}$$

$$\text{PEC(fulmar)} = 0.0001 \text{ µglead/µgMP} * 3430 \text{ µgMP/kgprey} = 0.343 \text{ µglead/kgprey} = 0.000343 \text{ mglead/kgprey}$$

Additivity of risk is assumed when more than one chemical is present in a case, which means that the RQs for individual chemicals are summed for copepod, cod and fulmar, respectively. Only priority substances in accordance with the Water Framework Directive and certain other pollutants are included in the analysis. This implies that 17 out of the approximately 50 identified chemicals are included, and the total risks are therefore underestimated. The extent of underestimation is however not known, as it requires knowledge of all EQS values.

RQs larger than one, indicating potential risk, is observed for the pelagic community (copepod and cod) and the flame-retardant PeBDE used in PUR, the biocide tributyltin used in PVC and PUR, and the flame-retardant hexabromocyclododecane (HBCD) use in EPS. The highest estimated RQ for fulmar and secondary poisoning is 0.1 for PeBDE used in PUR.

Production of PeBDE in the EU ceased in 1997. The most common use, accounting for 95-98% of PeBDE since 1999, has been in PUR, which may contain between 10 and 18wt-% of the PeBDE formulation (UNEP, 2006). The use of

PentaBDE was banned in the EU in 2004 through the Council directive 2003/11/EC relating to restrictions on the marketing and use of certain dangerous substances (SFT, 2009). Some recycling of articles containing these substances and produced before introduction of the ban cannot be excluded (Stockholm Convention, 2019b).

Tributyltins can be present as impurities in mono- and dibutyltin stabilisers up to 1wt-%, but their content was voluntarily controlled by industry to ≤ 0.67 wt-% (as tin). From July 2010 new products with >0.1 wt-% (as tin) were banned (Hansen et al., 2013).

HBCD is listed in Annex A to the Stockholm Convention (2019a) with specific exemption for production and use as flame-retardant in EPS and XPS in buildings until August 2017. After this date EPS and XPS may still occur in the environment and furthermore significant amounts of HBCD is present in recycled PS packaging (Abdallah et al., 2018).

Another chemical with a relatively high, but yet acceptable RQ (0.1) for copepod and cod is the softener bis-(2-ethylhexyl)phthalate (DEHP) that is used in PVC.

For the remaining additives, i.e. metals and organic compounds, monomers and methylene dianiline (MDA) a degradation product from methylene diphenyl diisocyanate (MDI) used in PUR, the estimated individual RQs and summed RQs are all below 0.08 indicating an additional margin of safety according to the conservative approaches used in this assessment.

Table 4 Cases 1-7 with polymer type, main product groups relevant to the marine environment. Estimated bioavailable amounts of residual monomers, degradation products and additives in weathered plastic particles.

Cases: Polymer type	Main product groups relevant to marine environment	Bioavailable amounts of residual monomers, reaction products and additive in weathered plastic particles/fragments in the marine environment. (CAS no) (wt-%)
1: Low-density polyethylene (LDPE)	Plastic bags, containers, bottles, tubing, personal care products and bud sticks	<p>Monomer: Ethylene (CAS no 9002-88-4) (0.001wt-%)</p> <p>Antioxidant: BHT (CAS no 128-37-0) (0.001wt-%)</p> <p>Antioxidant: BHEB (CAS no 4130-42-1) (0.001wt-%)</p> <p>Antioxidant: Isonox 129 (CAS no 35958-30-6) (0.001wt-%)</p> <p>Antioxidant: Irganox 1076 (CAS no 2082-79-3) (0.001wt-%)</p> <p>Antioxidant: Irganox 1010 (CAS no 6683-19-8) (0.001wt-%)</p> <p>Pigment: Lead sulfochromate yellow (CAS no 1344-37-2) (0.01wt-%)</p> <p>Additives: Paraffin wax (0.001wt-%)</p>
2: Styrene butadiene rubber (SBR)	Car tires	<p>Monomer: 1,3-butadiene (CAS no 106-99-0) (0.001wt-%)</p> <p>Monomer: Styrene (CAS no 7782-42-5) (0.001wt-%)</p> <p>Filler: Carbon black (CAS no 1333-86-4) (0.001wt-%)</p> <p>Accelerator: Zinc oxide (CAS no 1314-13-2) (0.001wt-%)</p> <p>Accelerator: Stearic acid (CAS no 57-11-4) (0.001wt-%)</p> <p>Vulcanizing agent: Sulphur (CAS no 7704-34-9) (0.001wt-%)</p> <p>Accelerator: N,N-diphenyl guanidine (CAS no 102-06-7) (0.001wt-%)</p> <p>PAHs: BaP (0.000005wt-%), BbF (0.000002wt-%), BkF (0.0000004wt-%), B(g,h,i)P (0.000018wt-%), I(1,2,3-cd)P (0.000007wt-%), anthracene (0.000004wt-%), fluoranthene (0.00004wt-%), naphthalene (0.000003wt-%)</p> <p>Metals: Lead (0.00005wt-%) and Nickel (0.00005wt-%)</p>
3: Acrylate polymers (Acrylics, polyacrylates)	Paints for ships and pleasure boats	<p>Monomer: Acrylic acid (CAS no 79-10-7) (approx. 0.0001wt-%)</p> <p>Copper (I) oxide (CAS no 1317-39-1) (0.5wt-%)</p> <p>Zinc ethylene-1,2-bis-dithiocarbamate (zineb) (CAS no 12122-67-7) (0.05wt-%)</p> <p>Tetraethyl silicate (CAS no 78-10-4) (0.03wt-%)</p> <p>Copper pyrithione (CAS no 14915-37-8) (0.03wt-%)</p> <p>Zinc oxide (CAS no 1314-13-2) (0.03wt-%) (0.25wt-%)</p> <p>Cupric oxide (CAS no 1317-38-0) (0.03wt-%)</p> <p>Copper (metallic) (CAS no 7440-50-8) (<0.001wt-%)</p>

Table 4 (continued)

4: Polyvinyl chloride (PVC)	Cables, cords, linoleum flooring also on ships	<p>Monomer: Vinyl chloride (CAS no 75-01-4) (0.00000001wt-%)</p> <p>Plasticizers: DEHP (CAS no 117-81-7) (0.35wt-%) and BBP (most toxic example) (CAS no 85-68-7) (0.15wt-%)</p> <p>Heat and UV stabilizers: Lead (0.0001wt-%), Cd (0.001wt-%)</p> <p>Pigments: Lead (0.01wt-%), Cd (0.001wt-%)</p> <p>Antimicrobial agent: OBPA (CAS no 58-36-6) (0.0005wt-%) or tributyltin (CAS no 688-73-3) (0.001wt-%)</p> <p>Antioxidant and UV stabilizer: Nonylphenols (CAS no 25154-52-3) (0.003wt-%)</p>
5: Polyurethane (PUR) rigid foam	Building insulation, construction material	<p>Reagent: Oligomer MDI (CAS no 32055-14-4) (0.001wt-%)</p> <p>Additive: C14-17 chloroalkanes (CAS no 85535-85-9) (0.01wt-%)</p> <p>Plasticiser and viscosity regulator: Tris(2-chlorisopropyl)-phosphate (CAS no 13674-84-5) (0.005wt-%)</p> <p>Flame-retardant: PeBDE (CAS no 32534-81-9) (0.15wt-%)</p> <p>Biocide: TBTO (CAS no 56-35-9) (0.001wt-%)</p> <p>Curing agent, cross-linker and chain extender: MOCA (CAS no 101-14-4) (0.001wt-%)</p> <p>Reaction product: MDA (CAS no 101-77-9) (1ppb=0.0000001wt-%)</p>
6: Expanded polystyrene (EPS) foam	Building insulation and packaging	<p>Monomer: Styrene (CAS no 7782-42-5) (0.005wt-%)</p> <p>Flame-retardant: HBCD (CAS no 25637-99-4) (0.01wt-%)</p> <p>UV stabilizer: Tinuvin P (CAS no 2440-22-4) (0.0001wt-%)</p> <p>UV stabilizer: Tinuvin 770 (CAS no 52829-07-9) (0.00006wt-%)</p> <p>Antioxidant: Wytox (CAS no 26523-78-4) (0.00001wt-%)</p> <p>Antioxidant: Irganox 1076 (CAS no 2082-79-3) (0.0001wt-%)</p>
7: Polycarbonate (PC)	Construction materials	<p>Monomer: Bisphenol A (CAS no 80-05-7) (0.001wt-%)</p> <p>Reagent: Diphenyl carbonate (CAS no 102-09-0) (0.001wt-%) or</p> <p>Reagent: Phosgene (CAS no 75-44-5) (0.001wt-%)</p> <p>Pigments: Lead (0.01wt-%)</p>

Table 5 Predicted Environmental Concentrations (PECs), Danish *Miljøkvalitetskrav* (MKK) and European Environmental Quality Standards (EQS) used as PNEC, and Risk Quotients (RQs) for the seven plastic cases. Only priority substances in accordance with the Water Framework Directive and certain other pollutants, are included. Estimated PECs for chemicals are based on exposures of plastic particles in marine water: 42 mgMP/m³, cod: 3.5 µgMP/kgbw/day and 700 µgMP/kgfood, fulmar: 1 gplastic/kgbw/day and 3430 µgplastic/kgprey. Chemicals with RQ>1 are marked in bold red.

Cases: Polymer type Chemical		PEC	PNEC	RQ = PEC/EQS
% chemical in weathered plastic				
1: LDPE	Lead (0.01wt-%)	Copepod: 0.0042 µgPb/L	Copepod: 1.3 ²⁾ µgPb/L	Copepod: 0.003
		Cod: 0.0042 µgPb/L	Cod: 1.3 ²⁾ µgPb/L	Cod: 0.003
		Fulmar: 0.00034 mgPb/kgprey	Fulmar: 3.6 ³⁾ mgPb/kgwwfood	Fulmar: 0.0001
2: SBR	BaP (0.000005wt-%)	Copepod: 0.0000021 µgBaP/L	Copepod: 0.00017 ²⁾ µgBaP/L (marker for PAHs)	Copepod: 0.012
		Cod: 0.0000021 µgBaP/L	Cod: 0.00017 ²⁾ µgBaP/L (marker for PAHs)	Cod: 0.012
		Fulmar: 0.0000002 mgBaP/kgprey	Fulmar: no data for sec. poisoning ⁴⁾	Fulmar: no
	Anthracene (0.000004wt-%)	Copepod: 0.000002 µgAnt/L	Copepod: 0.1 ²⁾ µgAnt/L	Copepod: 0.00002
		Cod: 0.000002 µgAnt/L	Cod: 0.1 ²⁾ µgAnt/L	Cod: 0.00002
		Fulmar: 0.00014 µgAnt/kgprey	Fulmar: 92222 ⁵⁾ µgAnt/kgwwbiota	Fulmar: 1E-09
	Fluoranthene (0.00004wt-%)	Copepod: 0.00002 µgFlu/L	Copepod: 0.0063 ²⁾ µgFlu/L	Copepod: 0.003
		Cod: 0.00002 µgFlu/L	Cod: 0.0063 ²⁾ µgFlu/L	Cod: 0.003
		Fulmar: 0.0014 µgFlu/kgprey	Fulmar: 11522 ⁶⁾ µgFlu/kgwwbiota	Fulmar: 1E-07
	Naphthalene (0.000003wt-%)	Copepod: 0.000001 µgNap/L	Copepod: 2 ²⁾ µgNap/L	Copepod: 6E-07
		Cod: 0.000001 µgNap/L	Cod: 2 ²⁾ µgNap/L	Cod: 6E-07
		Fulmar: 0.0001 µgNap/kgprey	Fulmar: 12266 ⁷⁾ µgNap/kgwwbiota	Fulmar: 8E-09
	Lead (0.00005wt-%)	Copepod: 0.000021 µgPb/L	Copepod: 1.3 ²⁾ µgPb/L	Copepod: 0.00002
		Cod: 0.000021 µgPb/L	Cod: 1.3 ²⁾ µgPb/L	Cod: 0.00002
		Fulmar: 0.000002 mgPb/kgprey	Fulmar: 3.6 ³⁾ mgPb/kgwwfood	Fulmar: 5E-07
	Nickel (0.00005wt-%)	Copepod: 0.000021 µgNi/L	Copepod: 8.6 ²⁾ µgNi/L	Copepod: 2E-06
		Cod: 0.000021 µgNi/L	Cod: 8.6 ²⁾ µgNi/L	Cod: 2E-06
		Fulmar: 0.0017 µgNi/kgprey	Fulmar: 12300 ⁸⁾ µgNi/kgwwbiota	Fulmar: 1E-07
	Zinc (0.001wt-%)	Copepod: 0.00042 µgZn/L	Copepod: 7.8 ¹⁾ µgZn/L (added to background)	Copepod: 0.00005
		Cod: 0.00042 µgZn/L	Cod: 7.8 ¹⁾ µgZn/L (added to background)	Cod: 0.00005
		Fulmar: 0.034 µgZn/kgprey	Fulmar: No value	Fulmar: No value
				<u>Sum RQ:</u>
				Copepod: 0.015
				Cod: 0.015
				Fulmar: 7E-07
3: Acrylate polymers	Zinc (0.05wt-% + 0.25wt-%)	Copepod: 0.126 µgZn/L	Copepod: 7.8 ¹⁾ µgZn/L (added to background)	Copepod: 0.016
		Cod: 0.126 µgZn/L	Cod: 7.8 ¹⁾ µgZn/L (added to background)	Cod: 0.016
		Fulmar: 10.3 µgZn/kgprey	Fulmar: No value	Fulmar: No value

4: PVC	Vinyl chloride (1E-08wt-%)	Copepod: 4E-09 µgVC/L Cod: 4E-09 µgVC/L Fulmar: 3E-07 µgVC/kgprey	Copepod: 0.05 ¹⁾ µgVC/L Cod: 0.05 ¹⁾ µgVC/L Fulmar: No value	Copepod: 8E-08 Cod: 8E-08 Fulmar: No value
	DEHP (0.35wt-%)	Copepod: 0.15 µgDEHP/L Cod: 0.15 µgDEHP/L Cod: 2.45 µgDEHP/kgfood Fulmar: 0.012 mgDEHP/kgprey	Copepod: 1.3 ²⁾ µgDEHP/L Cod: 1.3 ²⁾ µgDEHP/L Cod: 16000 ⁹⁾ µgDEHP/kgwwtfood Fulmar: 17 ⁹⁾ mgDEHP/kgfood	Copepod: 0.11 Cod: 0.11 Cod: 0.0002 Fulmar: 0.0007
	BBP (0.15wt-%)	Copepod: 0.063 µgBBP/L Cod: 0.063 µgBBP/L Fulmar: 5.1 µgBBP/kgprey	Copepod: 0.75 ¹⁾ µgBBP/L Cod: 0.75 ¹⁾ µgBBP/L Fulmar: No value	Copepod: 0.084 Cod: 0.084 Fulmar: No value
	Lead (0.0001wt-% + 0.01wt-%)	Copepod: 0.0042 µgPb/L Cod: 0.0042 µgPb/L Fulmar: 0.00035 mgPb/kgprey	Copepod: 1.3 ²⁾ µgPb/L Cod: 1.3 ²⁾ µgPb/L Fulmar: 3.6 ³⁾ mgPb/kgwwfood	Copepod: 0.033 Cod: 0.033 Fulmar: 0.0001
	Cd (0.001wt-% + 0.001wt-%)	Copepod: 0.00084 µgCd/L Cod: 0.00084 µgCd/L Fulmar: 0.00007 mgCd/kgprey	Copepod: 0.2 ²⁾ µgCd/L Cod: 0.2 ²⁾ µgCd/L Fulmar: 0.16 ¹⁰⁾ mgCd/kgwwfood	Copepod: 0.004 Cod: 0.004 Fulmar: 0.0004
	Arsen (0.001wt-%)	Copepod: 0.0004 µgAs/L Cod: 0.0004 µgAs/L Fulmar: 0.034 µgAs/kgprey	Copepod: 0.6 ¹⁾ µgAs/L (added to background) Cod: 0.6 ¹⁾ µgAs/L (added to background) Fulmar: No value	Copepod: 0.0007 Cod: 0.0007 Fulmar: No value
	Tributyltin (0.001wt-%)	Copepod: 0.00042 µgTBT/L Cod: 0.00042 µgTBT/L Fulmar: 0.034 µgTBT/kgprey	Copepod: 0.0002 ²⁾ µgTBT/L Cod: 0.0002 ²⁾ µgTBT/L Fulmar: 230 ¹¹⁾ µgTBT/kgwwprey	Copepod: 2.1 Cod: 2.1 Fulmar: 0.0001
	Nonylphenols (0.003wt-%)	Copepod: 0.0013 µgNP/L Cod: 0.0013 µgNP/L Fulmar: 0.0001 mgNP/kgprey	Copepod: 0.3 ²⁾ µgNP/L Cod: 0.3 ²⁾ µgNP/L Fulmar: 10 ¹²⁾ mgNP/kgbiota	Copepod: 0.004 Cod: 0.004 Fulmar: 0.00001
				<u>Sum RQ:</u> Copepod: >1 Cod: >1 Fulmar: 0.001
5: PUR	PeBDE (0.15wt-%)	Copepod: 0.063 µgPeBDE/L Cod: 0.063 µgPeBDE/L Fulmar: 5.1 µgPeBDE/kgprey	Copepod: 0.0049 ¹³⁾ µgBDE/L (polyBDE) Cod: 0.0049 ¹³⁾ µgBDE/L (polyBDE) Fulmar: 44 ¹³⁾ µgBDE/kgwwbiota (polyBDE)	Copepod: 12.9 Cod: 12.9 Fulmar: 0.116
	Tributyltin (0.001wt-%)	Copepod: 0.00042 µgTBT/L Cod: 0.00042 µgTBT/L Fulmar: 0.034 µgTBT/kgprey	Copepod: 0.0002 ²⁾ µgTBT/L Cod: 0.0002 ²⁾ µgTBT/L Fulmar: 230 ¹¹⁾ µgTBT/kgwwprey	Copepod: 2.1 Cod: 2.1 Fulmar: 0.0001

				<u>Sum RQ:</u> Copepod: >1 Cod: >1 Fulmar: 0.1
6: EPS	HBCD (0.01wt-%)	Copepod: 0.0042 µgHBCD/L Cod: 0.0042 µgHBCD/L Fulmar: 0.34 µgHBCD/kgprey	Copepod: 0.0008 ²⁾ µgHBCD/L Cod: 0.0008 ²⁾ µgHBCD/L Fulmar: 167 ¹⁴⁾ µgHBCD/kgwwbiota	Copepod: 5.3 Cod: 5.3 Fulmar: 0.002
7: PC	Bisphenol A (0.001wt-%)	Copepod: 0.00042 µgBA/L Cod: 0.00042 µgBA/L Fulmar: 0.034 µgBA/kgprey	Copepod: 0.01 ¹⁾ µgBA/L Cod: 0.01 ¹⁾ µgBA/L Fulmar: No value	Copepod: 0.042 Cod: 0.042 Fulmar: No value
	Lead (0.01wt-%)	Copepod: 0.0042 µgPb/L Cod: 0.0042 µgPb/L Fulmar: 0.00034 mgPb/kgprey	Copepod: 1.3 ²⁾ µgPb/L Cod: 1.3 ²⁾ µgPb/L Fulmar: 3.6 ³⁾ mgPb/kgwwfood	Copepod: 0.032 Cod: 0.032 Fulmar: 0.0001
				<u>Sum RQ:</u> Copepod: 0.07 Cod: 0.07 Fulmar: 0.0001

¹⁾ BEK no 1625; ²⁾ Directive 2013/39/EU; ³⁾ Lead EQS dossier 2011; ⁴⁾ PAH-5-6-rings EQS dossier 2011; ⁵⁾ Anthracene EQS dossier 2011; ⁶⁾ Fluoranthene EQS dossier 2011; ⁷⁾ Naphthalene EQS dossier 2011; ⁸⁾ Nickel EQS dossier 2011; ⁹⁾ DEHP summary risk assessment report 2008; ¹⁰⁾ EQS Substance data sheet Cadmium 2005; ¹¹⁾ EQS Substance data sheet TBT 2005; ¹²⁾ EQS Substance data sheet Nonylphenol 2005; ¹³⁾ PolyBDEs EQS dossier 2011; ¹⁴⁾ HBCDD EQS dossier 2011.

4. Discussion and outlook

4.1 Risk assessment of microplastic in the marine environment

There is still a long way to go to perform evidence-based decision-making with respect to exposure, effects, and risks posed by microplastic (MP) in the marine environment. The existing framework for environmental risk assessment, which is used in regulatory contexts worldwide, is yet to be applied to marine MP. Therefore, it is not possible to univocally demonstrate whether MP contamination poses a risk to the marine environment (Koelmans et al., 2017; Syberg et al., 2015).

Steps on the way have been to rank plastic polymer types and product use categories based on hazard classifications of monomers (Lithner et al., 2011; Groh et al., 2019), and recently an environmental risk assessment was performed of the direct effect of MP particles, but not of the indirect effects of associated chemicals (Everaert et al., 2018).

To elaborate further on the assessment by Everaert et al. (2018) it is necessary to know the type, size and number of MP and associated chemicals per unit volume of water taken in by organisms in order to answer how exposure varies through space and time, and to assess this relative to effect endpoints. It is no longer just the risk of a chemical or summed risks of chemicals, but a risk assessment of the plastic particle that undergoes changes as a consequence of weathering, together with its changing chemical constituents. In fact, Koelmans et al. (2017) argue that risk assessment of plastic debris should separate the risk component of the plastic associated chemicals from the risk component of the plastic material itself.

For a MP source there are thus basically three parameters, determining the risk that can be varied in multiple ways; plastic polymer type, chemical additives and product/activity. When dealing with such a complex problem, scoping is essential. This work has emphasized some of the most significant processes and data from manufacture of plastic product to effects and risks. It has outlined a framework for assessing the risk of residual chemical additives, monomers and their degradation products towards organisms from three trophic levels in the marine environment. Furthermore, it has considered the most probable plastic sources and polymer types to significantly affect to marine environment. All the while acknowledging that some important simplifications have been made.

4.2 Understanding fate

Accurate forecasting of transport from sources gives the spatial link in the risk assessment chain. As management and mitigation of MP pollution are costly, it becomes important to concentrate the effort where it has largest effect. Today quality-assessed ocean current forecasts and time series at medium scale resolution are available in all Danish marine areas (She et al., 2007; Berg et al., 2012; HBM; CMEMS), as well as matured litter-tracking software coupled to ocean currents (Christensen et al., 2018). This can and have been used routinely to assess transport scales of pollution released from localized sources (CLAIM; Zambianchi et al., 2017; Rossi et al., 2013). Transport modelling is a

cross-disciplinary field; while horizontal transport prediction is fairly well-established (Christensen et al., 2018), simulation of sedimentation, degradation and uptake pathways are more challenging, due to complexity of processes and uncertainty in process rates (Cozar et al., 2014).

The knowledge on settling of MP is still based on only a handful of studies and it is still unknown to what extent low-density MP will be incorporated into aggregates and settle to the seabed and there is a clear need for further studies of the inter-particle dynamics and interaction between MP and other suspended material in natural freshwater and marine environments. There is similarly a need for studies of the dynamics of the broad range of different types of MP particles composed of different polymer types. The extent and timescale of biofouling of MP with living cells is also largely unknown and there is a need for studies of this, both in situ and in controlled laboratory settings.

For recycled plastic, it may be the case that non-intentional additives that are sorbed from the environment and from the waste handling processes are carried along in the recycling process. It needs to be investigated whether they will be more prevalent and critical towards the marine environment than what could be expected for intentional additives in “clean” plastic material.

4.3 Leaching and effects on marine organisms

A study performed in this project on the effects on common coastal zooplankton species exposed to increasing concentrations of new and old car tire particles, showed that the feeding and pellet production (combined measure of feeding and assimilation) of zooplankton were influenced by concentration and type of MP, food level and zooplankton species. The results indicated complex interactions of plastic properties, abiotic factors and plankton communities, which need to be taken into account when estimating the effects of MP pollution in the marine environment.

The metric used to quantify the effect should be ecologically relevant and should be the same as the one used to quantify exposure. For conventional chemicals, this ecologically relevant metric is the concentration (Koelmans et al., 2017). As mentioned above, the exposure concentration consists of both a MP concentration and a chemical concentration. Weathered MP may not change in concentrations by mass, whereas the associated chemicals may change considerably in species and concentration. This is essential to bear in mind, for example when performing risk assessment of ingested MP in the stomach of fulmars. Some of the plastic particles may be similar to the original plastic material and some may be weathered. The chemical constituents and thereby chemical risks may be very different.

Furthermore, when quantifying the concentration of MP in marine organisms it is often done by visual inspection. Limitations are identifying MP smaller than approx. 2 mm, and distinguishing MP from natural debris and not detecting MP in the gut of ingested prey. This can lead to considerable underestimations of ingested MP. However, Hertzke et al. (2016) conclude that bioaccumulation of POPs by fulmars is mainly governed by the ingestion of natural prey. POPs taken up via ingested MPs may equilibrate readily in the intestines of the birds, making a negligible contribution to accumulation, yet absorbing POPs from the ingested food simultaneously such that POP profiles in plastic

reflect the profiles observed in tissues. Hertzke et al. (2016) furthermore investigated the contribution of plastic additives to bioaccumulation and concluded that since many of these chemicals are not present in the environment in the same concentrations as POPs sorbed from the environment, the relative significance of plastic associated additives must be included when calculated the summed chemical risk to marine species. It is also concluded that the effects on enhanced mass transfer of chemicals sorbed to the material, i.e. increased leachability, as a consequence of direct contact of the MP with digestive fluids in the digestive tract and stomach of the organisms, are not yet fully understood.

4.4 Toxicity of chemicals and polymers

This study used MKK and EQS as PNEC for priority substances within the Water Framework Directive and certain other pollutants. Priority substances only comprise a limited number of the total considered chemicals. To obtain a more complete quantification of the chemical risk all, or the most important, chemicals must be considered. This requires some effort in terms of compiling relevant toxicity values such as EC50 or NOEC and assign assessment factors to derive PNECs. Additivity of chemical risk can be assumed, and also the risk of the MP itself must be considered.

For the plastic particle itself, polymers are often not considered hazardous (EC, 2012). However, tentative 'effect' thresholds for MPs have been recently proposed for the marine environment by various authors. However, the Dossier Submitter has concluded there is currently insufficient information to derive a robust PNECs for MPs, that could be used to justify a conclusion that risks are adequately controlled, either based on current exposures in the environment or exposures that are forecast to occur in the future (ECHA, 2019b).

4.5 Analytical methods

There is no single analytical method that is able to quantify all polymers in a sample. Of the methods available, the FTIR-based methods are the most versatile in terms of identifying polymer types. Raman-based methods can also determine the materials which FTIR can, but does have some issues with fluorescence of particles. It does furthermore only look at the very surface of the particles and is hence more readily affected by particle coating or overlapping. Neither of the approaches can determine car tire debris, for which thermos desorption based methods, for example pyrolysis-GC-MS, are suited. A benefit of the two spectroscopic methods (FTIR and Raman) is that they allow a simultaneous determination of particle number, size, and shape. When applied together with imaging, the methods also allow particle mass estimations. The thermal desorption methods, on the other hand, only allow mass to be quantified. Sizes must hence be determined through fractioning prior to analysis, for example a cascade sieving. The size limits of the methods allow (standard) FTIR to quantify particles go down to 5-10 μm (identification without quantification can be down to 2-3 μm), while Raman can go a bit lower, with identification without quantification around 1 μm . Pyrolysis-GC-MS is in principle particle independent. However, the sample preparation methods need to allow extraction, purification, and concentration of the particles, which hitherto is undocumented for the very fine particles (say, below 10 μm).

The methods used to identify MP have improved greatly in the past few years. However with these improvements has come challenges in the form of data

handling and processing. The development of new software such as MPhunter that is capable of automating significant portions of this data analysis can increase the amount of identification that can be carried out while reducing the time spent conducting it. The continued development of this analytical software and its increased implementation has the potential to speed up analysis of MP in environmental samples.

The methods are in principle at a level where monitoring can be attempted. However, the methods applied by the different labs are not standardized and do not yield the same results when analyzing identical samples. On the other hand, if a lab applying state-of-the art methods apply the same analysis repeatedly on the same sample, it is now possible to get reasonable agreement between the analyses. It should hence also be possible to inter-calibrate labs using identical methods. If the labs use methods that differ in the protocols – and especially the analytical quantification – it is quite uncertain whether such agreement can be expected.

4.6 Nano plastics

Over time, plastics will degrade from micro-size fragments to nano-size fragments in the environment due to ageing and weathering. The risk associated with such nanoscale-materials and –fragments is understood much less than risk associated with conventional chemicals (Scott-Fordsmand et al. 2016). Hence, to get a sufficient understanding of risk, studies must be conducted with materials identical or similar to the nano-sized fragments and to what is leached from the plastic. This calls for longer-term experiments being conducted (e.g. Gonçalves et al. 2017) with weathered plastic fragments, in which nanomaterials are embedded. It is important that the fragments are allowed to weather fully in the test-systems in order to mimic what happens in nature. If weathering does not take place, the experiment may show a lack of biological effect, even in cases where a biological effect would be present in the longer term. For example, biological experiments often start with large fragments (e.g. larger than 100 nm), because it is difficult to obtain homogenous samples of smaller fragments, and the test duration (e.g. 28 days) does not allow most polymers to be degraded sufficiently to release embedded material. Even in the absence of effects, such experiments cannot be used to conclude on the potential long-term impact of plastic fragments. The way forward is to develop suitable analytic techniques for complex environments (although this may take a long time) to develop long-term hazard tests that can include the long-term degradation of the plastics. This should cover all life cycles of the materials.

4.7 Data availability

Considering the complex underlying construct of MP in the marine environment, the availability of high quality data is a big challenge. To do more detailed studies of the processes that are known to be of importance more data are needed. Therefore, it is a situation where scoping of the studies is essential, and that the evolving knowledge eventually will form a basis that is complete and strong enough to be able to reliably predict risk.

Generating and implementing data as a collaboration between science and industry must be emphasised. Combining bottom up and top down approaches often introduce missing links between data and information from different sources. This link is information on types and amounts of used additives,

which is typically confidential. The Danish downstream distributors and manufacturers do not have access to this information, and somehow a way forward to work around confidentiality and be able to assess information about content must be found, in order to link plastic products with the specific chemical formulas used in these.

However, new data is being generated continuously these years in scientific studies, and in work such as the ECHA (2019) mapping of plastic additives.

4.8 What is needed to make the risk assessment more correct and complete?

In order to enhance the information level and improve the environmental risk assessment of MP and nano-size particles, a wide set of improvements could be suggested. These are listed below for a number of elements forming the necessary basis of the risk assessment.

From production:

- Improved identification of additives that must be in focus, e.g. from the developing ECHA site
- Additives used in specific products

In the external environment:

- Characterization and quantification of environmental (weathered) plastic particles:
 - Polymer types and amounts
 - Persistence to weathering processes (microbial, solar radiation, thermal oxidation)
 - Flocculation and sedimentation
- Identification and quantification of chemicals, linked with polymer type, and dependence of weathering of plastic particles:
 - Residuals of monomers, additives and degradation products
 - Sorbed environmental chemicals (vector effect)
- Further development of quality assured, standardized measurement techniques

Inside the organism:

- Determination of uptake and elimination rates of plastic particles and associated chemicals
- Determination of role of plastic in gut:
 - Dilution of chemical concentration (sorption)
 - Increased chemical concentration (vector effect and desorption)
- Quantification of the effects (PNEC or EQS) on marine organisms of:
 - Chemicals
 - Weathered polymer

When risk assessment is improved, regulation/substitution is facilitated with respect to chemicals, polymers and product types.

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RISK ASSESSMENT OF HARMFUL TYPES OF PLASTICS IN THE MARINE ENVIRONMENT

This report presents the results of a risk assessment of residual chemical additives, monomers and degradation products present in microplastic (MP) particles in the marine environment. Seven cases of different polymer types and product groups are defined that represent the most significant exposures of MPs, and thus potential high-risk cases towards marine organisms. Risk Quotients (RQ) are calculated for three trophic levels, i.e. pelagic/planktonic zooplankton: copepod, benthopelagic fish: atlantic cod and seabird: northern fulmar. Danish Miljøkvalitetskrav (MKK) and European Environmental Quality Standard (EQS) values are used as toxicity threshold values. RQ larger than unity, which indicates potential risk, is estimated for copepod and cod (pelagic community) and the flame-retardant pentabromodiphenylether (PeBDE) used in polyurethane (PUR), the biocide tributyltin (TBT) used in polyvinylchloride (PVC) and PUR, and the flame-retardant hexabromocyclododecane (HBCD) used in expanded polystyrene (EPS). The highest estimated RQ for fulmar (secondary poisoning) is 0.1 for PeBDE used in PUR.